On the density calculation of fabricated zirconia toughened alumina by unconventional method

Sudip Kundu, Subhrojyoti Mazumder, Supradeepa Panual G, Kunal Ghosh and Nilrudra Mandal*
CSIR-Central Mechanical Engineering Research Institute, Durgapur, West Bengal-713209, India
E-mail: *n_mandal@cmeri.res.in

Abstract. Aim of the paper is to fabricate zirconia toughened alumina (ZTA) by varying compaction pressure and sintering temperature from commercially available ZTA powder in the laboratory and postulate an unconventional method for estimating the bulk density in the zirconia toughened alumina (ZTA) apart from conventional Archimedes principle method. The operating parameters have been selected to investigate the void fraction at different sintered conditions. The densities of the as sintered specimens are estimated from the micrograph taken at different positions of the specimens with the help of image processing method using field emission scanning electron microscopy (FESEM). The results are compared with the conventional one and found a deviation of minimum and maximum of ~3.34 and ~5.95 % respectively. The said method can be considered for approximating the voids more precisely since during the conventional Archimedes method, the medium remains unable to reach into the core of each pore completely. At higher temperature the grain growth increases which in turn densifies the overall composite structure and thus leading to the pore reduction.

1. Introduction
Development of advanced ceramic components is replacing the conventional material component due to its promising mechanical properties like fracture toughness, high hardness, flexural strength etc [1-3]. Among the wide application field of such materials in Cutting tool manufacturing, automotive, aerospace industries etc., fabrication of cutting tool inserts is one of the ever emerging areas of deploying ceramics into the industrial application [4-7]. The mechanical properties of a bulk component are dependent on the porosity of the structure and the porosity can be controlled by varying the sintered temperature and pressure [8-14]. Bagga et al. derived that with the elevated temperature, the adatoms mobility increases which favours their diffusions of the grain boundaries, hence packing density between the particles are increased [15]. Reyes-Rojas et al. analysed the microstructure of carbon nano-tube-reinforced ZTA at uniaxial pressing, cold isostatic pressing (CIP), and pressureless sintering methods and concluded that the relative density for the cold isostatic and uniaxially pressed composites were approximately the same, although CIP treated ZTA shows a significant improvement in other mechanical properties [16]. Inside a sintered product, the pores structures are also dependent on the particles size and this is why, the uniform particle size has been taken [17]. Norfauzi et al. proved that due to low density of pure alumina, it shows more fragile property than zirconia toughened alumina since the bonding energy at the grain boundary is very low due to high porosity of pure alumina [18].

The measurement of density by different method is debateable. Archimedes principle by water displacement is the most conventional method for measuring the density. However, this method may not be reliable in every instance since flushing is required to fill the pores again, particularly near the closed geometry [19]. Along with that bubbles could not be removed from the grain boundaries of the sintered particles. This is why repeatability is too low in this conventional method. In contrast to this Archimedes method, image processing method is very much reliable when it comes to repeatability [20]. It shows profound consistency when the density is measured by processing the image at different portion of the specimens. Therefore, bulk density measurement method by image
processing has close value as well as precise [21]. Khodaei et al. calculated the elastic modulus of titanium scaffolds analytically which is quite different from the experimentally measured value due to its porosity [22].

The current work aims to investigate the close value density and the subsequent apparent porosity of the laboratory fabricated ZTA samples by considering a range of operating parameters viz., compaction pressure (520, 607 and 694 MPa) and sintering temperatures (1550, 1600 and 1650°C). The present model could help to better understand the density range on temperature and pressure effect of sintered ZTA and provide a new method to describe the porosity of sintered ceramics which can also help us better understand the behavior and performance of porous ceramics at high temperature and pressure. The work follows two different approaches to evaluate the densities and apparent porosities of the as sintered samples: 1. Archimedes principle and 2. Image processing method. The later stage of the work describes the significance differences between the results coming out using these two different techniques. Earlier research evidences that at maximum pressure and temperature the grain growth is better than other specimens. When the ZTA particles shift from one position to another because of the compaction, atomic diffusions via surface occur which leads to particle sintering or coarsening. These processes increase the adjacent particle bond and strength which causes the change of pore morphology [23]. The process of sintering of ZTA takes place into three phases. In the first stage, the relative density is only 65-70% due to necking and in the second later stage the densification takes place up to 90%. This second stage is the reason for making isolated pores from the continuous pores. Due to the formation of these isolated pores, it is impossible to calculate the density by Archimedes principle. In the final stages, main grain growth takes place which depends on the active diffusion process. Inside the growing grains, occlusion of pores takes place due the enhanced grain growth which is the reason of the lower density at higher temperature and pressure.

2. Materials and Method

2.1 Fabrication of the specimens

The ZTA specimens are fabricated in the laboratory via powder metallurgy route by the cold press technique. The properties of the commercially available powder are given in the table 1. The unprocessed ZTA powder is first milled in high energy planetary ball mill (FRITSCH, Pulverisette 5) using alumina balls (10 mm diameter) in acetone medium for 30 hrs. The slurry is oven dried at 100°C for 10 hrs.

![Fabrication steps](image)

Figure 1. Different steps of specimen fabrication

The dried mixture is then ground in mortar pestle in order to get fine powder particle. The fine powder is sieved through 180µm sieve shaker to eliminate the bigger particles. The final powder is compacted into circular pellets of thickness 3.5 mm and diameter 10 mm by uniaxial press (CARVER, Indiana USA) at three pressure levels 520, 607 and 694 MPa. The compacted pellets are sintered in high temperature furnace at the temperatures 1550, 1600 and 1650 °C by maintaining a dwell time 1 hour for each. The various stages of the specimen preparation are depicted in the figure 1. Figure 2 shows the final fabricated specimens for performing the tests.
Table 1. Properties of the commercial ZTA powder

| Property           | Values                  |
|--------------------|-------------------------|
| Primary particle size | ~1 μm                  |
| Bulk density       | 0.43 g/cm^3             |
| Supplier           | Zirox technologies, India |

2.2 Bulk density measurement approach in porous ZTA specimen

It is impossible to fabricate a sintered product without porosity. Henceforth, it is required to distinguish the density corresponding to the existing pores. A bulk sample includes both the open pores and closed pores. However, the true volume does not include any pores. From the relation between bulk density and true density we can calculated the porosity of a porous structure [24, 25].

\[
\text{Porosity} = \frac{(D_{\text{true}} - D_{\text{bulk}})}{D_{\text{bulk}}} \tag{1}
\]

\[
D_{\text{bulk}} = \frac{M}{V_{\text{bulk}}} \tag{2}
\]

\[
\text{and } D_{\text{true}} = \frac{M}{V_{\text{true}}} \tag{3}
\]

Where, \(M\) is the mass, \(V\) is the volume and \(D\) is the density of the specimen.

We have followed two separate methods to compare our results. First approach is Archimedes principle and the second one is by image processing. The true density to calculate the porosity was quoted from the literature as 4.55 g/cm^3 [26].

2.2.1 Measurement of bulk density using Archimedes principle. In our research, the bulk densities of the nine specimens of ZTA are measured using Archimedes principle [27, 28]. The procedure to measure the density is the following:

a) First, the dry weight (\(W_1\)) is need to measured.

b) Then, the weight of the specimen in water (\(W_2\)) is required to measure by hanging the specimen with a wire of diameter 1 mm. The weight of the wire is also required to subtract from this measured value.

c) After taking out the sample from water, the weight of the sample is measured in the air. This weight is the water saturated weight (\(W_3\)) of the specimen. The density of the water at 27°C has been taken 0.9965 g/cm^3. The weight loss of the specimen in water is (\(W_3-W_2\)).

\[
\text{Density} = \frac{(\text{Dry weight of sintered sample})}{(\text{Weight loss in water})} \times 0.9965 \text{ g/cm}^3 \tag{4}
\]

2.2.2 Measurement of bulk density by image processing approach. To evaluate the pores automatically, the micrographs are required to convert into binary images. FESEM images were taken to identify the pores and the structural density. Then, the FESEM images were changed into TIFF format with an 8 bit quantization and addressed to image processing after taking the resolution of 600 × 800 pixels. Multiple images were taken from random location in the specimens for repeatability.
The procedures of this quantitative study for segmentation of the images were done by ImageJ open source software consisting of the four steps which are pre-processing, threshold determination, binarization and morphological analysis [29-31].

a) In the first step, disturbing element should be removed from the original acquired images and segmented particle should be found to maximize the contrast between pores boundary.

b) In the threshold determination, the metal is changed to a single grey scale (e.g. white) and pores are changed to a different grey scale (e.g. black). In the ideal cases, to distinguish the pores easily, the pixel intensity threshold value is required to determine.

c) After determining the threshold level, the binary images are obtained, having pixel intensity set to 0 in the background and to 1 to the porous region. The number of image processing steps to reduce the noise is depends on the image quality.

d) Finally, morphological analysis was done on the binary images to calculate the percentage of void structures in the sintered specimens.

Then, to further segment parts or remove regions imprecisely segmented due to the noise, morphological filter is needed to apply. In our research, after the image processing, the digital representation of porous microstructures of the cross section are represented by the black areas in the images as shown in the figure 3. The ZTA specimens are designated as Z and the corresponding pressure and sintering temperature are written in the suffix.

2.3 Microstructural and metallurgical analysis
The microstructures of the as sintered specimens are investigated with the help of FESEM (ZEISS, Germany). Different phases of the alumina and zirconia ceramic composites are identified by means of X-ray diffraction analysis (X’Pert PRO, PANalytical B.V., PW3040/60, The Netherlands).
Figure 3. FESEM images of sintered ZTA specimens (a) and (b) Z520-1550; (c) and (d) Z607-1550; (e) and (f) Z694-1550; (g) and (h) Z520-1600; (i) and (j) Z607-1600; (k) and (l) Z694-1600; (m) and (n) Z520-1650; (o) and (p) Z607-1650; (q) and (r) Z694-1650 (left) and after image processing (right) the digital representation of porous microstructures of the cross section are represented by the black areas in the images.

3. Results and discussion
3.1 Comparison between the Archimedes and the image processing results
It has been shown from the graphs that the density value calculated from Archimedes principle is between 4.226 g/cm$^3$ and 4.440 g/cm$^3$ whilst the density value by image processing is 4.003 g/cm$^3$ and 4.264 g/cm$^3$. The reason behind this difference is because of the Archimedes principle it is impossible for us to fill the inner pores of a sintered sample and also most of the time inner bubble is difficult to remove. Thus, the value is smaller than the original value. The density increases as the temperature and pressure rises. The deviation is maximum (5.95%) at 607 MPa and 1600 °C. The porosity is maximum when the temperature is 1550 °C and the pressure is 520 MPa and minimum at 1650 °C and 694 MPa. Table 2 demonstrates the density and porosity values for all specimens obtained from the Archimedes principle and the image processing method.
Figure 4. Influence of sintering temperature and pressure on density of sintered ZTA (a) Archimedes Principle (b) Image processing

Table 2. Bulk density and porosity values for each specimen.

| Sl No. | Specimen       | Bulk density by Archimedes principle (g/cm³) | Bulk density by image processing method (g/cm³) | % deviation | Calculated porosity (%) | Porosity by image processing (%) |
|--------|----------------|---------------------------------------------|-----------------------------------------------|-------------|------------------------|----------------------------------|
| 1      | Z520_1550      | 4.266 ± 0.010                               | 4.033 ± 0.015                                 | 5.46        | 6.24                   | 11.36                            |
| 2      | Z607_1550      | 4.276 ± 0.020                               | 4.123 ± 0.045                                 | 3.57        | 6.02                   | 9.38                             |
| 3      | Z694_1550      | 4.305 ± 0.004                               | 4.137 ± 0.040                                 | 3.90        | 5.38                   | 9.07                             |
| 4      | Z520_1600      | 4.344 ± 0.014                               | 4.113 ± 0.091                                 | 5.31        | 4.52                   | 9.60                             |
| 6      | Z694_1600      | 4.412 ± 0.008                               | 4.244 ± 0.051                                 | 3.80        | 3.03                   | 6.72                             |
| 7      | Z520_1650      | 4.338 ± 0.015                               | 4.133 ± 0.061                                 | 4.72        | 4.65                   | 9.16                             |
| 8      | Z607_1650      | 4.397 ± 0.007                               | 4.25 ± 0.053                                  | 3.34        | 3.36                   | 6.59                             |
| 9      | Z694_1650      | 4.440 ± 0.018                               | 4.264 ± 0.051                                 | 3.96        | 2.41                   | 6.28                             |

3.2 Effect of simultaneous pressure and temperature on the bulk density
The FESEM micrographs show no potential grain growth in the micrographs below 1650 °C and corresponding density is almost constant in this range. Furthermore, when the pressure increases at 1650 °C, the grain size also increases and the compaction between the particles is much better. Subsequently, the density increases. Although, we have observed that from the graphs that the rate of density increase is much higher between 1550 °C to 1600 °C and between 1600 °C and 1650 °C, there are no such changes in density due to temperature. From the images, authors have concluded that the pressure effect is the only reason of the grain growth between the temperature differences of 1600 °C to 1650 °C. Due to the high pressure, local plastic deformation between the compacted particles takes place at their contact point, if the yield strength at the respective temperature is attained by external pressure. Thus, hierarchical growth of the particles by sliding and rotation will be a reason for the densification during the isolated pore formation stage. Since the hardness of ZTA ceramic composite is very high, during sintering process softening and local melting causes the rearrangement and reduces the density.

The XRD pattern of the specimens compacted at 694 MPa and sintered at the different temperatures are shown in figure 5. The highest peak for the tetragonal phase was found in the case of Z694-1650 at 2θ = 320 as compared to others. It signifies the maximum volumetric expansion of the zirconia phases occurred at 1650 °C since there is higher intensity of the tetragonal phases and more the chances of metastability for transformation of tetragonal to monoclinic phases. Higher the volumetric expansion
more the chances of pores reduction. This might be reason why the density was maximum at the extreme temperature (1650 °C) and pressure (694 MPa).

Figure 5. XRD pattern of the specimens (a) Z694-1550, (b) Z694-1600 and (c) Z694 1650.

4. Conclusion
The present study is concerned with the bulk density calculation of the porous ZTA specimen using unconventional method. The Archimedes principle method for evaluating the bulk density has some limitations because of the improper voids fulfilment of the medium since the voids contain some entrapped air. In this work, the proposed technique for measuring the voids is found suitable alternative of the conventional Archimedes method to evaluate the bulk density more precisely. The deviation in the density result between these two methods is found to be in the range of 3.34% to 5.95%. Therefore, it can be concluded that this image processing method can be deployed to calculate the voids more minutely by taking into account the FESEM images of the micro pores as well. At high compaction pressure (694 MPa) and sintering temperature (above 1600 °C), it causes the plastic deformation in the particle boundaries and as a consequent, the interconnectivity between the pores reduces and isolated are pores generate and henceforth the overall porosity of the specimen decreases.

Acknowledgments
The authors would like to express their sincere thanks to the project Nanomission (SR/NM/NT-1062/2015), Department of Science and Technology (DST), Govt. of India, for the financial support.
References

[1] Besisa DH, Ewais EM, Ahmed YM, Elhosiny FI, Fend T and Kuznetsov DV 2018 Thermal shock resistance of pressureless sintered SiC/AlN ceramic composites Mater. Res. Express 501 5506

[2] Bauer J, Hengsbach S, Tesari I, Schwaiger R and Kraft O 2014 High-strength cellular ceramic composites with 3D microarchitecture Proc. National Acad. Sci.111 2453-8

[3] Jang BK and Sakka Y 2007 Thermophysical properties of porous SiC ceramics fabricated by pressureless sintering Sci. Technol. Adv. Mater.8 655-659

[4] Sommer F, Talpeanu D, Kern F, Gadow R and Heisel U 2015 Medium Density Fiberboard Machining and Wear Behavior of Injection- Molded Ceramic Composite Wood Cutting Tools Int. J. Appl. Ceram. Technol. 12 147-56

[5] Bensoulia H, Aouici H, Meddour I, Yallese MA, Mabrouki T and Girardin F 2016 Performance of coated and uncoated mixed ceramic tools in hard turning process Measurement 82 1-18

[6] Shalaby MA, El Hakim MA, Abdelhameed MM, Krzanowski JE, Veldhuis SC and Doshaeva GK 2014 Wear mechanisms of several cutting tool materials in hard turning of high carbon–chromium tool steel Tribol. Int.70 148-54

[7] Sktani ZD, Azhar AZ, Ratnam MM and Ahmad ZA 2014 The influence of in-situ formation of hibonite on the properties of zirconia toughened alumina (ZTA) composites Ceram. Int.40 6211-7

[8] Bocanegra-Bernal MH, Dominguez-Rios C, Echeberria J, Reyes-Rojas A, Garcia-Reyes A and Aguilar-Elguezabal A 2017 Effect of low-content of carbon nanotubes on the fracture toughness and hardness of carbon nanotube reinforced alumina prepared by sinter, HIP and sinter+ HIP routes Mater. Res. Express 4 085004

[9] Schumacher TC, Treccani L and Rezwan K 2015 Effect of silica on porosity, strength, and toughness of pressureless sintered calcium phosphate–zirconia bioceramics Biomed. Mater.10 045020

[10] Kurgan N 2014 Effect of porosity and density on the mechanical and microstructural properties of sintered 316L stainless steel implant materials Mater.Des. 55 235-41

[11] Dargatz B, Gonzalez-Julian J and Guillon O 2015 Improved compaction of ZnO nanoparticles triggered by the presence of acetate and its effect on sintering Sci. Technol. Adv. Mater.16 025008

[12] Guo S and Kagawa Y 2012 High-strength zirconium diboride-based ceramic composites consolidated by low-temperature hot pressing Sci. Technol. Adv. Mater.13045007
[13] Bakhsh N, Khalid FA and Hakeem AS 2014 Effect of sintering temperature on densification and mechanical properties of pressureless sintered CNT-alumina nanocomposites IOP Conf. Ser. Mater. Sci. Eng. 60 012059

[14] Toghyani S and Khodaei M 2018 Fabrication and characterization of magnesium scaffold using different processing parameters Mater. Res. Express 5 035407

[15] Bagga S, Akhtar J and Mishra S 2018 Influence of porosity on the properties of nanostructured tin oxide thin film Mater. Res. Express 5 116406

[16] Reyes-Rojas A, Domínguez-Ríos C, García-Reyes A, Aguilar-Elguezabal A and Bocanegra-Bernal MH 2018 Sintering of carbon nanotube-reinforced zirconia-toughened alumina composites prepared by uniaxial pressing and cold isostatic pressing Mater. Res. Express 5 105602

[17] He D, Wang S, Liu R, Wang Z, Xiong X and Zou J 2018 Experimental study on pore structure and performance of sintered porous wick Mater. Res. Express 5 026506

[18] Norfauzi T, Hadzley AB, Azlan UA, Faiz MM, Naim MF and Aziz AA 2018 Comparison machining performance of Al2O3, ZTA and ZTA doped Cr2O3 cutting tools on AISI 1045 Mater. Res. Express 6 016547

[19] Adams GJ, Cook RB, Hutchinson JR and Zioupos P 2018 Bone apparent and material densities examined by cone beam computed tomography and the Archimedes technique: comparison of the two methods and their results Front. Mech. Eng. 3 23

[20] Lee JC and Ahn SH 2018 Bulk density measurement of porous functionally graded materials Int. J. Precis. Eng. Manuf. 19 31-7

[21] Haeri M and Haeri M 2015 ImageJ plugin for analysis of porous scaffolds used in tissue engineering J. Open Res. Software 3 1-4

[22] Khodaei M, Fathi M, Meratian M and Savabi O 2018 The effect of porosity on the mechanical properties of porous titanium scaffolds: comparative study on experimental and analytical values Mater. Res. Express 5 055401

[23] Chaim R, Chevallier G, Weibel A and Estournès C 2018 Grain growth during spark plasma and flash sintering of ceramic nanoparticles: A review J. Mater. Sci. 53 3087-105

[24] Spierings AB, Schneider M and Eggenberger R 2011 Comparison of density measurement techniques for additive manufactured metallic parts Rapid Prototyping Journal 17 380-6

[25] Keenan MJ, Hegsted M, Jones KL, Delany JP, Kime JC, Melancon LE, Tulley RT and Hong KD 1997 Comparison of bone density measurement techniques: DXA and Archimedes' principle J. Bone Miner. Res. 12 1903-7
[26] MatWeb Material Property Data. Available from: www.matweb.com

[27] Pul M 2019 Effect of sintering on mechanical property of SiC/B4C reinforced aluminium Mater. Res. Express 6 016541

[28] Kundu S, Hussain M, Kumar V, Kumar S and Das AK 2018 Direct metal laser sintering of TiN reinforced Ti6Al4V alloy based metal matrix composite: Fabrication and characterization Int. J. Adv. Manuf. Technol.97 2635-46

[29] Re GL, Lopresti F, Petrucci G and Scaffaro R2015 A facile method to determine pore size distribution in porous scaffold by using image processing Micron 76 37-45

[30] Ross L and Russ JC 2011 The image processing handbook Microsc. Microanal. 17 843

[31] Rajagopalan S, Lu L, Yaszemski MJ and Robb RA 2005 Optimal segmentation of microcomputed tomographic images of porous tissue- engineering scaffolds J. Biomed. Mater. Res. Part A 75A 877-87