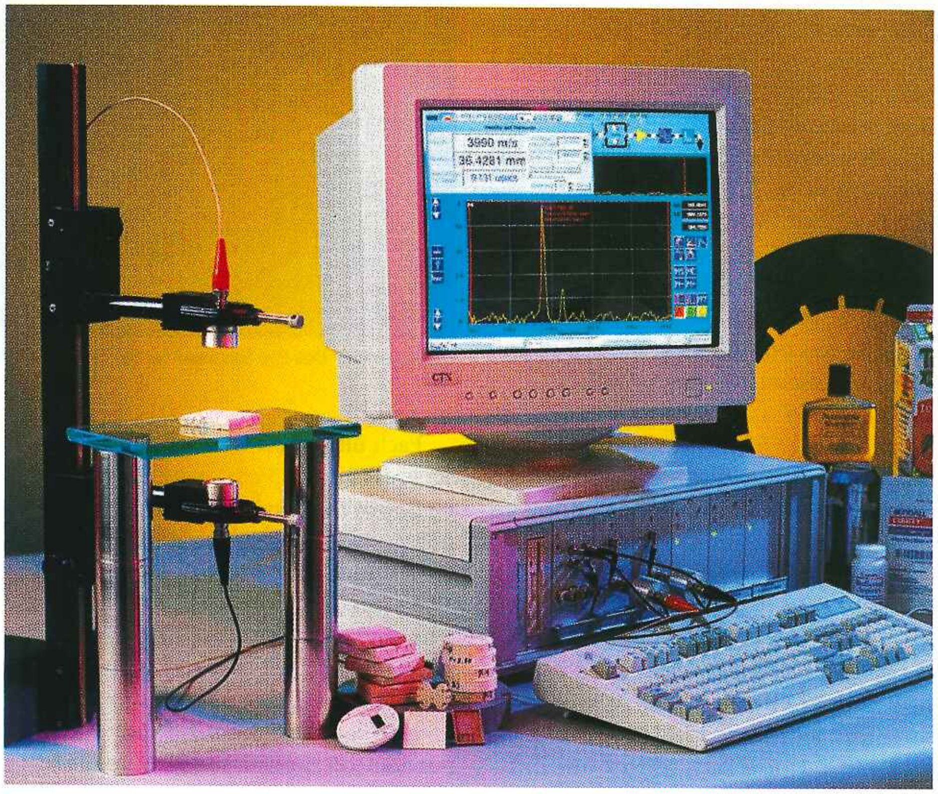
MEASURING GREEN BODY Density

by **P. Pei, M. C. Bhardwaj, J. Anderson, D. Minor and T. Thornton**

Bulk density is defined as the total mass of a body divided by the bulk volume. For the purposes of this article, the bulk volume is defined as all space that is interior to the macroscopic "envelope" surface of the body. For a green body, the bulk volume includes the volume of solid particles, the volume of any temporary additives and liquid present, and the volume of empty pore space.[1]

The bulk density of a green ceramic body provides valuable information needed to control the quality of a ceramic piece (after firing) with respect to its final size and the porosity and cracks in the body. Therefore, it is important that optimum measurement procedures to be followed in determining density.[2]

Many American Society for Testing and Materials (ASTM) methods for determining bulk density of refractory materials and glasses are described in annual books published by ASTM (see www.astm.org). Most of these methods are based on volume displacement by Archimedes' principle; that is, since both refractory materials and glasses are compatible with water, their bulk density can be easily determined by volume displacement in water. However, this test method is not suitable for green body ceramics, which will disintegrate easily in water. For green body ceramics, mercury pycnometry is recognized as the benchmark method for measuring the bulk volume of a body. Mercury is an excellent displacement liquid—its high wetting angle and large surface tension prevents it from penetrating the small pores in green bodies. However, mercury has a high toxicity and is considered to be a significant health hazard. Mercury porosimetry is currently used (a) to generate bulk density data to be compared with data obtained from other absolute measurement techniques and (b) to generate calibration standards for a relative measurement technique.



Noncontact (air coupled) ultrasound determines ultrasound velocity through a material with approximately 10 mm of air between the specimen and the transducers.

In 1999, an assessment report on several laboratory techniques for bulk density measurement was published.[1] The techniques studied include mercury pycnometry (ASTM C493-93), water displacement of bodies coated with wax (ASTM C914-95) or with a water repellent spray, volume displacement of mineral oil, and powder pycnometry methods. Of all measurement techniques studied with a limited number and shape of samples, the compacted powder pycnometry appeared to be promising when compared to mercury pycnometry.

Experimental Procedures

Green Ceramic Bodies Studied

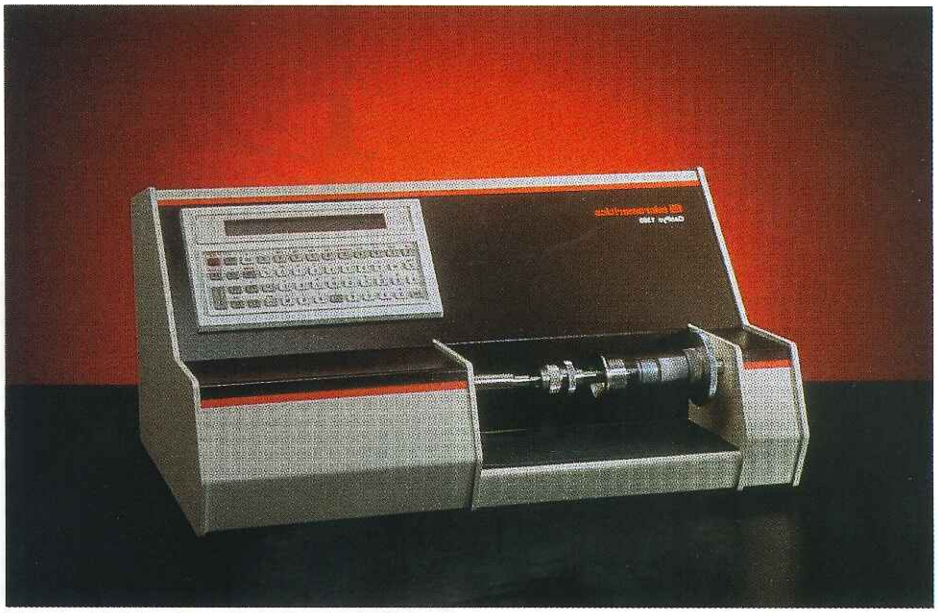
Green body samples with different preparation procedures were used in this study. The first set of alumina samples was prepared by using a uniaxial pressing process in different sized pressing dies at various pressures. The second set of samples comprised commercial alumina and electronic porcelain tiles.

The first pressed alumina samples were cylinders, and GE 94ND2 was the alumina powder used. Pressed alumina cylinders with a dimension of 1.86 cm (0.75 in.) height and 1.28 cm (0.5 in.) diameter were designated as the "A" series. The pressures used were 142 MPa (20.5 Kpsi), 85.0 MPa (12.3 Kpsi), 56.6 MPa (8.21 Kpsi) and 35.4 MPa (5.13 Kpsi). Altogether, 24 cylinders were produced with six cylindrical samples at each pressure setting. Their green body densities were first determined by the mass-volume measurement technique, and the density value (g/cm^3) at each pressure was approximately 2.22, 2.15, 2.10 and 2.04, respectively. Thus, a range of densities was produced for the higher precision measurements that follow.

The second set of alumina samples, designated as the "B" series, was pressed uniaxially with the same alumina powder, but they were in disc form. Their dimensions were 3.15 cm (1.25 in.) diameter and 0.9 cm (0.36 in.) thick. The pressing loads were 32.3 MPa (4.68 Kpsi), 48.4 MPa (7.02 Kpsi), 64.5 MPa (9.35 Kpsi) and 96.8 MPA (14.038 Kpsi). Their densities (g/cm^3) at each pressure by mass and volume measurement technique were approximately 1.96, 2.05 2.11 and 2.19, respectively.

These two sets of alumina samples were used to compare the bulk densities determined by mercury porosimeter, compact powder pycnometry, and the mass-volume measurement technique. The bulk densities obtained from the mass-volume method were used to establish correlation with noncontact ultrasound measurements.

Two sets of 9 cm x 9 cm (3.5 in. x 3.5 in.) square alumina tile samples were also studied. The first set consisted of two electronic porcelain tile samples, designated "C" and "D," and were pressed at 12.6 MPa (1825 psi) 18.1 MPa (2625 psi), respectively. The second set consisted of two 96% alumina tile samples, designated "E" and "F," and were pressed at 12.6 MPa (1825 psi) and 18.1 MPa (2625 psi), respectively.



Micromeritics' Geo-Pyc was used for the compacted powder measurements.

Each tile sample was cut into nine small squares (3 cm x 3 cm), which were examined with the noncontact ultrasound technique and numbered Al to A9. After ultrasound study, each tile sample was cut again into nine smaller squares (1 cm x 1 cm), and the edges were shaped to fit the porosimeter's cell (penetrometer), which was not large enough to hold the first divided samples (3 cm x 3 cm). Mercury porosimeter measurements were made on three of the 1 cm x 1 cm samples, and the average of the three measurements was taken as the corresponding noncontact ultrasound measurement.

After obtaining both their ultrasound velocity data at these nine positions of each tile sample and then their corresponding bulk density values by mercury porosimeter, a correlation between the two techniques was considered to determine whether noncontact ultrasound velocity can be used as a relative measurement technique for bulk density gradient of each tile sample.

Bulk Density Measurement Methods

Mercury displacement method. Two mercury porosimeter instruments were used in this study. The Autoscan Porosimeter (Quantachrome Corp., Boynton, Fla.) was used to measure the bulk densities of the alumina tile samples, and the AutoPore Ill mercury porosimeter (Micromeritics Instrument Corp., Norcross, Ga.) was used to measure the bulk densities of the alumina discs.

For both porosimeters, a penetrometer with known volume was used. The cell tapered into a finer tube at one end where a reference mark is present for accurate filling. The volume of mercury displaced by the green body is determined by measuring the following masses: the mass of the green body (WB), the mass of the cell filled with mercury (WC+Hg), and the mass of the cell filled with mercury plus the green body (WC+Hg+B). The mass of mercury displaced by the green body is equal to (WC+H9) - (WC+Hg+B - WB). By keeping the temperature constant during the measurements, the density of mercury is known, with which the volume of mercury displaced is calculated knowing the mass. The bulk density of the green body is the mass of the green body divided by the displaced mercury volume.[1,3]

Compacted powder method. In this method, a packing of fine powders serves as the displacement media. The volume of a body is measured by the change in volume of a given quantity of particles before and after the body is immersed in the particles under the same applied force.[1,3] The instrument used here was the Geo-Pyc from Micromeritics Instrument Corp. Parametric studies of the instrument have been reported previously.[1]

To improve the repeatability and reproducibility of the method, the following parameters should be carefully considered: consolidating force, ratio of sample volume to the chamber volume, sample shape, sample position in the chamber, and pretest sample preparation in the instrument.

Mass-volume measurement. Since the alumina cylinders and discs have geometric shapes, the volume can be calculated from a few linear measurements. A digital caliper can measure the lengths, thicknesses and diameters needed for the calculation to obtain the volume of cylindrical and circular bodies. An analytical balance can obtain mass of the green bodies, and bulk densities can be derived.

For tile samples, the edges of the divided tile subsamples are not perfect, so linear measurements are not possible. Therefore, mass-volume measurements are not feasible.

Noncontact ultrasonic measurements. Noncontact (air coupled) ultrasound, a relatively new technique to characterize green bodies,[4,5] determines ultrasound velocity through a material with approximately 10 mm of air between the specimen and the transducers. Since it is a noncontact technique, measurements on fragile samples such as green body ceramics can be made. Before this new technique, ultrasound velocity through a sample was generally measured in a medium such as water, and it is impossible to immerse green ceramics in water without disintegration.

Noncontact ultrasound is a relative method and has the potential to be used as a nondestructive quality control technique to control green body density during an on-line production process, since it can perform precise measurements at a speed of 20 readings per second.

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For the tests discussed in this article, ultrasonic velocities were measured with the NCA 1000 noncontact analyzer from Secondwave Systems Corp, Boalsburg, Pa. This system is characterized by >140 dB dynamic range and a time-of-flight uncertainty of ±20 ns (under open ambient air condition) and ±1 ns (under closed condition)—i.e., uncertain measurements can be improved 20 times under closed conditions. After routine calibration, the NCA 1000 measures thickness, velocity, time-of-flight and attenuation of the test material. The transducers used in these tests were the nominally high transduction noncontact type that are nominally 1 MHZ and have a 12.5 mm active area diameter. Since the transducer probe is relatively small (app. 12.5 mm diameter), bulk density gradients can be monitored within a ceramic piece.

Results

Comparison of Green Body Density Measurements on Alumina Cylinders

For the alumina cylinders, green body density was measured by both the mass-volume method and powder compacted pycnometry. Bulk density measurements by the mass-volume method were determined at three laboratories: NIST, University of New Mexico and Secondwave System Corp. The values are in agreement to the first decimal place. However, the variation of three sets of mass-volume data shows that the method is operator-dependent.

The density values between powder compacted pycnometry values and the mass-volume values are also in agreement to the first decimal place, but the repeatability of the powder compacted pycnometry is good to the second decimal place.

Comparison of Green Body Density Measurements on Alumina Discs

For the alumina discs, bulk body density measurements were generated by three methods: mass-volume, powder compacted pycnometry and mercury porosimeter. The agreement between the values was good to the second decimal place.

Correlation Between Green Body Density Measurements and Ultrasound Velocity Measurements

Noncontact ultrasound velocity measurements were also made on these two sets of samples. Since both cylinders (A series) and discs (B series) are composed of the same alumina powder and uniaxially pressed, the correlation between bulk density by the mass-volume method and ultrasound velocity measurements should hold for both samples. The correlation coefficient for these samples (R2) was 0.88. The good correlation observed in this study illustrated the possibility of using noncontact ultrasound velocity measurements as a relative method for bulk densities.

Comparison of Green Body Density Measurements on Alumina Tiles

For the set of commercial tile samples, there were two objectives for this study: 1) to establish the correlation between bulk densities by mercury pycnometer and noncontact ultrasonic velocities, and 2) to illustrate the possibility of using noncontact ultrasound method as a nondestructive evaluation method to study bulk density gradients within a green body, such as a tile.

The good correlations observed between the bulk density measurements of the subdivided tiles and their noncontact ultrasonic velocities illustrate the possibility of using noncontact ultrasonic velocity measurements as a nondestructive evaluation method for density gradient measurements, since the detection area of the transducer diameter is only 12.5 mm. The correlation coefficient between densities and ultrasound velocities of the two tile samples are 0.77 for the electronic porcelain tiles and 0.91 for the 96% alumina tiles.

Conclusions

Bulk densities of well defined samples such as discs and cylinders can be determined by both mass-volume measurements and powder displacement pycnometry instruments, and their values are comparable to those measured with a mercury porosimeter. For complex-shaped green body samples, a more detailed study still needs to be done with powder displacement pycnometry instruments.

Noncontact ultrasound velocity measurements are promising as a relative method for measuring bulk density, including density gradient measurement, within well defined green samples such as discs and cylinders. The noncontact measurement also has the potential to be an on-line quality control technique. However, it is a relative method, and bulk density standards of the same ceramics with known bulk density values are needed to calibrate the noncontact ultrasound instrument. Work is in progress at NIST to develop bulk density and porosity standards for the calibration purpose of future relative methods.

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