JOURNAL OF MATERIALS SCIENCE **37** (2002) 2557–2561

The impact of water impregnation method on the accuracy of open porosity measurements*

YIM-BUN P. KWAN[‡], J. R. ALCOCK
School of Industrial and Manufacturing Science, Cranfield University,
Cranfield, Bedford, MK43 0AL, UK
E-mail: j.r.alcock@cranfield.ac.uk

Open porosity is one of the most important parameters in the characterisation of a porous ceramic. Two methods based on the Archimedes' Principle, ISO 2738 and EN623-2 are currently used as standards for the measurement of open porosity. The method in ISO 2738 was found to underestimate the open-pore content, especially in fine-pored ceramics. In contrast, the EN623-2 method was found to more accurately measure the true open-pore content of the materials. A mathematical model to describe the phenomenon is proposed.

1. Introduction

Open porosity is an important parameter in the characterisation of porous ceramics. The most commonly used measurement method is based on the Archimedes' buoyancy principle [1], and requires the specimen to be fully impregnated with a fluid of known density, from which the total open pore volume is calculated. The methodology for this measurement technique is outlined in both the ISO 2738 standard [2] and in the European Standard EN623-2 [3]. The two standards differ essentially only in the method of impregnating the open pores with a fluid of known density.

In the ISO method, the specimen is impregnated with fluid by depressurising and then repressurising the specimen whilst it is immersed in the fluid. The standard is meant for porous metals and proposes oil as the impregnation fluid. This is often adapted for use in ceramics by using deionised water, which possesses a lower surface tension than oil and is more easily removed from the specimen after measurement.

Whilst this standard has been widely adopted, various authors have noted that the method lacks both reproducibility and accuracy. The density of the impregnating fluid limits reproducibility, as does its molecular size in relation to pore size [4]. The accuracy is limited by the efficiency with which the open pore network is filled by the impregnating fluid. One common modification [5] to the method in order to improve impregnation is the addition of a surfactant to the fluid to reduce the resistance to impregnation caused by surface tension.

Another approach is to use a lower surface tension fluid, such as xylene or toluene [6]. However, these methods result in only modest increases in the volume of open porosity measured and hence in accuracy.

A new method of improving the fluid impregnation has been proposed in the EN623-2. The method differs from the ISO method in that the specimen is evacuated *before* it is placed in the fluid and then repressurised when fully submerged.

In the following, a theoretical model is proposed to explain the physical phenomena that occur in both impregnation procedures. Mathematical equations are proposed to predict the resulting error in open porosity measurement. This is followed by experimental verification of the improvement in accuracy.

2. Theory

2.1. Evacuation in the fluid and atmospheric re-pressurisation (ISO 2738)

Consider a porous specimen immersed in a fluid as shown in Fig. 1. At equilibrium a meniscus will form within each surface pore across which the pressure drop from the Laplace equation [7] is equal to $4\gamma/d$, where d is the diameter of the pore and γ is the liquid-vapour surface tension of the impregnation fluid.

The pressure at the surface of a porous specimen is equal to the sum of the pressure external to the fluid, the hydrostatic pressure due to the column of water above the specimen and the Laplace pressure drop at the meniscus. After 'complete' evacuation the external pressure equals the evacuation pressure p_{evac}, and the pressure in the pore network (p_{p1}) is therefore:

$$p_{p1} = \rho_f g h_f + \frac{4 \cdot \gamma}{d_{surf}} + p_{evac} \tag{1}$$

where ρ_f is the fluid density, g is gravitational acceleration, h_f is the mean submerged depth of the specimen, and d_{surf} is the surface pore diameter.

---

*Based in part on the dissertation submitted by Y. B. P. Kwan for the degree of Ph.D., Cranfield University, Cranfield, Bedfordshire, United Kingdom, 1997.

[‡] *Present Address*: Siemens Dematic AG, Dept. SD EA 1 R&D 6, Rupert-Mayer-Str. 44, D-81359 Munich, Germany.

0022–2461

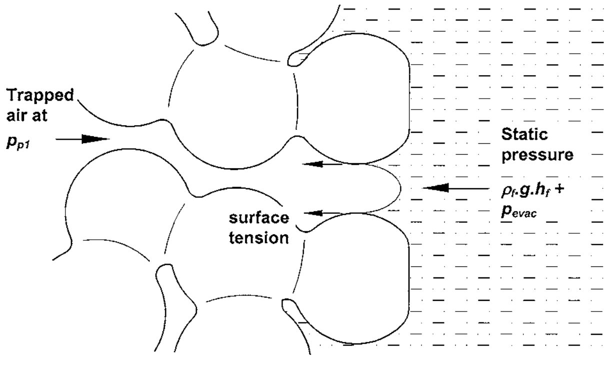

Figure 1 Static pressure within pore in submerged degassing (ISO 2738).

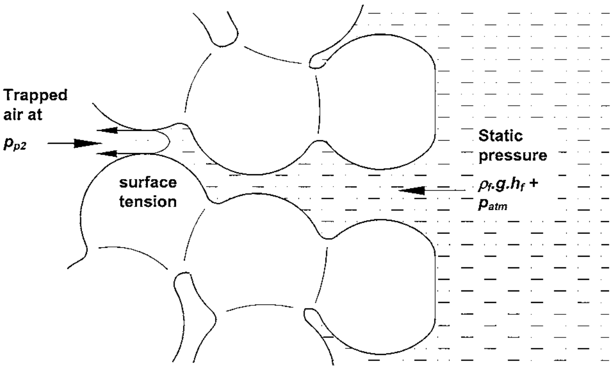

Figure 2 Static pressure within pore during repressurisation.

During depressurisation, the menisci stay at the surface pores. Therefore, in order for p_p to decrease to its final value in Equation 1, whilst the volume of porosity remains constant, air bubbles are expelled from the specimen. Assuming that all the pores are interconnected[§], the largest surface pore therefore, determines residual pressure in the submerged sample, as this corresponds to the lowest pressure drop acting against the expulsion of air. Hence, the value of d_{surf} in Equation 1 is equal to that of the largest surface pore of a porous ceramic specimen.

When water is used as the impregnation fluid, the surface tension component is the most dominant in Equation 1. The evacuation pressure is limited by the vapour pressure of water to approximately 2.5 kPa at 20°C [8]. A depth of 30 mm of water above the specimen would contribute 0.29 kPa to Equation 1. In contrast, for a specimen with a largest surface pore of 20 μm, the pressure drop due to the surface tension of water (72.7 mN m^{-1} at 20°C [8]) would be 14.5 kPa.

When atmospheric pressure is restored, the pressure in the pores is raised to a level near but not equal to atmospheric pressure. This occurs by a reduction in the volume of air within the specimen. Fluid enters the open capillary network under the action of both the external atmospheric pressure and surface tension. The fluid-vapour boundary now lies within the specimen as shown in Fig. 2, its position governed by the pore size distribution of the specimen. Hence, a reasonable approximation is that the pressure drop owing to surface tension is dependent on the mean pore size within the porous structure, d_{mean}. The residual air pressure in the pores that are not filled with the impregnation fluid is therefore:

$$p_{p2} = \rho_f g h_f + \frac{4 \cdot \gamma}{d_{mean}} + p_{atm} \tag{2}$$

Assuming air behaves as a perfect gas and compression takes place isothermally[¶], the volume of residual air left in the pores after repressurisation, V_{res}, can then be determined by:

$$V_{res} = \frac{p_{p1}}{p_{p2}} V_o^t \tag{3}$$

where V_o^t is the true open pore volume.

This residual volume will appear in the calculations as apparent closed porosity. The ratio V_{res}/V_o^t therefore represents the theoretical measurement error in open porosity due to incomplete impregnation alone.

2.2. Unsubmerged evacuation prior to atmospheric pressure impregnation (EN623-2)

Equation 3 can be rewritten as

$$\begin{aligned}\frac{V_{res}}{V_o^t} &= \frac{p_{p1}}{p_{p2}}\\ &= \left(\rho_f g h_f + \frac{4\gamma}{d_{surf}} + p_{evac}\right) \Bigg/ \\ &\quad \left(\rho_f g h_f + \frac{4\gamma}{d_{mean}} + p_{atm}\right)\end{aligned} \tag{4}$$

Equation 4 implies that V_{res} can be minimised if h_f, p_{evac}/P_{atm} and the surface tension of the fluid, γ, are all minimised on evacuation but are all maximised on repressurisation. This suggests that a more efficient alternative to the ISO 2378 method would be to carry out the evacuation step when the sample is not immersed in the impregnating fluid, as described in EN623-2. The sample would subsequently be immersed by flooding the vacuum chamber with water, before the start of repressurisation. As no liquid would be present on evacuation, Equation 4 would simplify to:

$$\frac{V_{res}}{V_o^t} = \frac{p_{evac}}{4\gamma/d_{mean} + p_{atm} + \rho_f g h_f} \tag{5}$$

Equation 5 implies that fluid impregnation would be nearest to complete when the mean pore size approaches zero and the surface tension of the impregnation fluid is high. Hence, the accuracy of the EN623 method would increase for fine pored materials using water as the impregnating fluid.

[§] If the specimen contains closed porosity, it plays no part in the weight gain in either of the two methods of impregnation.

[¶] The heat capacity of a porous material with a porosity level of ≤0.4, together with that of the impregnated fluid, is in general much higher than that of any residual air content still trapped. Thus, it is reasonable to assume that the air temperature remains constant during the compression.

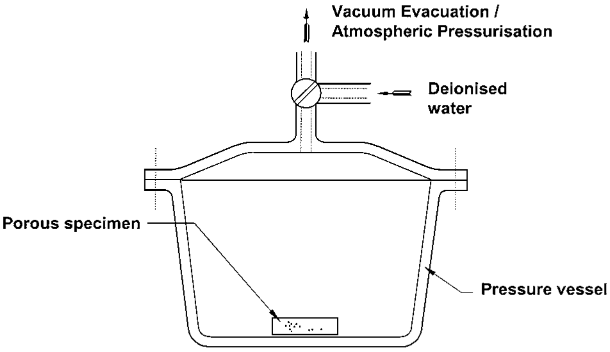

Figure 3 The equipment for water impregnation.

3. Experimental procedure

3.1. Test methods

In order to verify the theory as outlined above, a series of experiments was undertaken on characterised porous alumina samples. Three different test procedures were used, as detailed below:

Method 1: submerged degassing as per the ISO 2738 standard with deionised water as impregnation fluid.

Method 2: submerged degassing as per the ISO 2738 standard with xylene as impregnation fluid.

Method 3: unsubmerged degassing, repressurisation in deionised water to atmospheric pressure as per EN623-2 standard.

The test procedures followed the ISO2738 and EN623-2 standards. The density of fully dense alumina was taken as 3950 kg m^{-3} [9]. The test temperature was held at 20°C for each specimen. The height of the water column above the impregnated specimen was kept constant at 30 mm. A diagram of the test equipment is shown in Fig. 3.

Each method was used on each sample, except for method 2. A single set of measurements was carried out using xylene as the impregnation medium. This measurement technique was deemed irreproducible[**] as it was found that xylene evaporation significantly affected the mass measurements of the fluid-impregnated samples.

The ISO 2738 technique requires measurements of the dry mass of a porous specimen, m_1, the mass of the specimen when fully impregnated with the fluid, m_2, and the fully impregnated mass whilst suspended in the fluid, m_3.

The open pore volume is then calculated using:

$$V_o = \frac{m_2 - m_1}{\rho_f} \tag{6}$$

where the density of the impregnating fluid is ρ_f.

The fraction of open porosity ζ_o is found from the ratio between the open pore volume V_o and the total volume V_t:

$$\zeta_o = \frac{V_o}{V_t} \tag{7}$$

As discussed in Section 2, the empirically obtained value of ζ_o is dependent on the measurement technique and therefore ζ_o is described here as the apparent open porosity fraction. V_t is calculated from the mass measurements by:

$$V_t = \frac{m_2 - m_3}{\rho_f} \tag{8}$$

If the true density of the material specimen ρ_m is also known, the total porosity ζ_t, i.e., the sum of the open and closed porosity, can then be found from:

$$\zeta_t = 1 - \frac{m_1/\rho_m}{V_t} \tag{9}$$

and hence the closed porosity is:

$$\zeta_c = \zeta_t - \zeta_o \tag{10}$$

In order to calculate the theoretical predictions of apparent open porosity, the true open pore volume fraction, ζ_o^t, was required for each specimen. This was calculated from the experimental values of method 3, correcting the residual volume using Equation 5:

$$\zeta_o^t = \zeta_o^3 \bigg/ \left(1 - \frac{p_{evac}}{4\gamma/d_{mean} + p_{vac} + \rho_f g h_f}\right) \tag{11}$$

where ζ_o^3 is the apparent open porosity fraction calculated from method 3.[††] The surface tension and density of water were corrected to the experimental conditions.

Using method 3, the residual air volume for each test specimen was found to be less than 0.5% of total open pore volume.

The theoretical apparent open porosity fraction, ζ_o', was then calculated for the other impregnation methods by:

$$\zeta_o' = \zeta_o^t \cdot \left(1 - \frac{V_{res}}{V_o}\right) \tag{12}$$

where $\frac{V_{res}}{V_o}$ was determined for methods 1 & 2 from Equation 4. Values of mean pore and maximum surface pore diameters used in the calculations were the measured values as shown in Table I.

3.2. Specimen characterisation

Specimens for the test procedures outlined above were produced from 99.7% pure calcined, milled α-alumina [Alcan Chemicals Europe] powders of mean particle size between 6 and 23 μm, using the capsule-free hot isostatic pressing method first developed by Ishizaki [10]. The samples have a total porosity fraction ranging between 0.13 and 0.4. The specimens were diamond ground to approximately 45 mm in diameter and 6 mm thick, and ultrasonically cleaned in ethanol.

[**] Impregnated weight with xylene changes rapidly due to evaporation of the impregnating fluid.

[††] In the absence of any means of perfect pore impregnation, method 3 has been shown to have the highest impregnated weight implying that it is the least inaccurate. Results from method 3 compare well to porosity values determined from weight and volume [external dimensions] measurements assuming zero closed porosity.

TABLE I Geometrical details of porous alumina specimens

Specimen	A	B	C	D
Outside dia. (mm)	43.98	45.95	47.95	48.98
Thickness (mm)	4.25	6.86	6.96	7.34
Mean particle size (μm)	6.25	22.6	22.6	12.2
d_{mean} (μm)	0.41	0.99	1.23	2.35
d_{surf} (μm)	1.6	8	12	25

d_{mean} is the mean pore diameter, d_{surf} is the largest surface pore size. Specimens B and C, though the same particle size, have been sintered under different conditions to give different pore sizes.

The mean pore size, d_{mean}, of each specimen was determined using the improved dynamic water expulsion method developed by Gélinas [11]. This has the advantage that the same liquid medium is used as in the porosity measurement, and hence guaranteeing coherence of the surface tension effect at the pore-liquid interface in both measurements. The water expulsion method is, however, limited in pore size range (0.5 to 25 μm) which constrained the choice of experiment samples.

The largest surface pore of each specimen, d_{surf}, was determined using the reverse bubble point method [12]. Air was supplied to a specimen that was totally submerged in deionised water at a pressure sufficient to cause air bubbles to continuously form on the sample surface. The pressure was then reduced in steps of 0.5 kPa until the last bubble ceased to appear. The equivalent diameter of largest surface pore was then calculated using the bubble point equation from the relevant ISO standard, ISO 4003 [13].

A summary of the characterisation details of the specimens is given in Table I.

4. Results and discussion

Experimentally determined values of the apparent open porosity fraction of specimens A to D, ζ_o, are listed in Table II. Table II also lists the theoretically predicted values of apparent open porosity fraction, ζ'_o, according to the mathematical descriptions of methods 1 to 3 given in Section 2.

TABLE II Theoretical and experimental porosity values

Specimen	A	B	C	D	Method
V_t (cm^3)	6.44	11.13	12.32	13.75	From method 3
ζ_t	0.131	0.191	0.218	0.388	Based on V_t
ζ_o	0.051	0.157	0.200	0.388	method 1
	0.063	–	–	–	method 2
	0.074	0.173	0.213	0.392	method 3
ζ_o^t	0.074	0.173	0.213	0.392	Based on method 3 and Equation 5
ζ_c	0.057	0.018	0.005	−0.004	
ζ'_o	0.057	0.157	0.198	0.370	method 1
	0.067	–	–	–	method 2
	0.074	0.173	0.213	0.392	method 3
$(\zeta_o^t - \zeta_o)/\zeta_o^t$	0.311	0.092	0.061	0.010	method 1
	0.149	–	–	–	method 2
	0	0	0	0	method 3

A comparison of the values of ζ'_o and ζ_o in Table II shows that good agreement is obtained between the theoretical and experimental apparent open porosity fractions, demonstrating the validity of the proposed physical model. Furthermore, a comparison of ζ_o for the three test methods indicates that the unsubmerged evacuation method of water impregnation (method 3) was most effective in improving the accuracy of open porosity measurements, increasing the measured value for each specimen. As proposed by the theoretical hypothesis, the most significant improvement in accuracy of open porosity measurement occurred for specimens with small mean pore sizes (specimens A and B). This is indicated in Table II by the values for the fraction of true open porosity that is not measured, $(\zeta_o^t - \zeta_o)/\zeta_o^t$, which is greater for specimens A and B when measured by method 1.

Fig. 4 plots the predicted fraction of impregnated pores, $1 - V_{res}/V_o^t$, calculated from Equations 4 and 5, against the mean pore size of a ceramic specimen. Two examples of curves are presented for the ISO standard method showing the predicted completeness of impregnation for specimens with $d_{mean} : d_{surf}$ ratios of 1 : 4

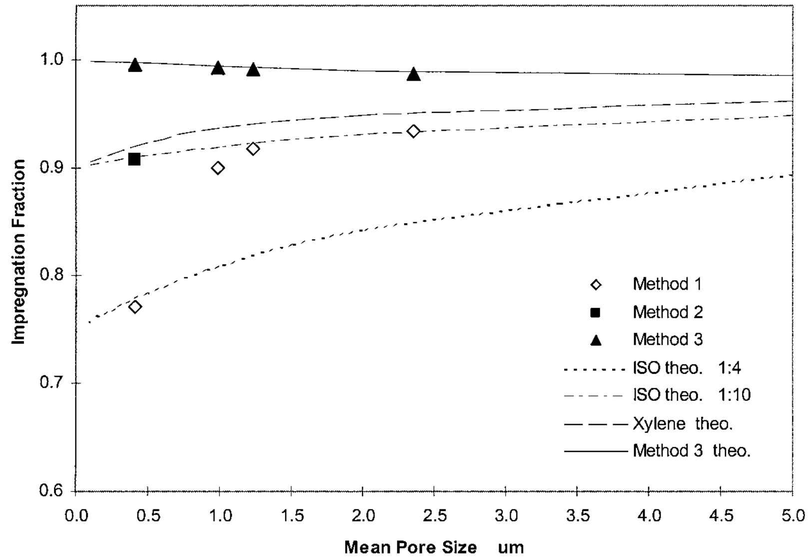

Figure 4 Comparison of predicted and experimentally determined fraction of impregnation.

and specimens with ratios of 1 : 10. For each ratio the predicted fraction of impregnated porosity decreases with mean pore size. For specimens with the same mean pore size, decreasing d_{surf} strongly decreases the predicted impregnated fraction. This is because the resistance by surface tension to the evacuation of the specimen during submerged evacuation is increased. In contrast the pore size and the $d_{mean} : d_{surf}$ pore size ratio play no role in unsubmerged evacuation.

Superimposed on the curves are the experimentally obtained data for specimens A to D, from methods 1 to 3. There is excellent agreement between the data points and the predicted trends. As shown in Table I, specimen A had a $d_{mean} : d_{surf}$ ratio of approximately 1 : 4 and in Fig. 4 its method 1 impregnation lies on the predicted ISO 1 : 4 curve. Specimens B to D had a $d_{mean} : d_{surf}$ ratio of approximately 1 : 10 and lie on the appropriate ISO curve. The method-3 data-points all lie within 0.015 of complete impregnation.

5. Conclusions

The measurement method for open porosity based on ISO 2738 was found to underestimate the open-porosity content, due to incomplete impregnation of the open pore volume. A mathematical model to describe the phenomenon has been established. Correlation with experimental data indicates that the model is effective in predicting the level of inaccuracy in the ISO method. An alternative method of water impregnation, as proposed in EN623-2, was found to offer a significant improvement of the accuracy of the open porosity measurement compared to the former.

The ISO method is most inaccurate for small-pored materials impregnated using a high surface tension fluid. However, accuracy is much improved in the EN method under the same conditions. One can conclude that the latter is a superior technique for the characterisation of fine-pored ceramics.

Acknowledgements

The authors would like to acknowledge Dr Roger Morrell of the NPL Materials Centre, National Physical Laboratory, United Kingdom for his helpful comments concerning this manuscript.

References

1. ARCHIMEDES, “Floating Bodies”.
2. ISO 2738, “Permeable Sintered Metal Materials—Determination of Density, Oil Content and Open Porosity” (1987).
3. EN623-2, “Advanced Technical Ceramics—Determination of Density and Porosity” (1993).
4. L. ZOU, R. D. BLOEBAUM and K. N. BACHUS, *Med. Eng. Phys.* **19**(1) (1997) 63.
5. S. M. FAVIER, M.Sc. thesis, Cranfield Institute of Technology, 1990.
6. A. TAKATA, K. ISHIZAKI, Y. KONDO and T. SHIOURA, *Mat. Res. Soc. Symp. Proc.* **251** (1992) 133.
7. R. FINN, “Equilibrium Capillary Surfaces” (Springer-Verlag, New York, 1986).
8. D. R. LIDE (ed.), “CRC Handbook of Chemistry and Physics,” 75th edn. (CRC Press, Boca Raton, FL, 1994).
9. R. MORRELL, “Handbook of Properties of Technical Engineering Ceramics, Part 1,” 1st edn. (HSMO, London, 1989).
10. K. ISHIZAKI and M. NANKO, *J. Por. Mat.* **1**(1) (1995) 19.
11. C. GÉLINAS and R. ANGERS, *Cer. Bull.* **65**(9) (1986) 1297.
12. Y. B. P. KWAN, Ph.D. thesis, Cranfield University, 1996.
13. ISO 4003, “Permeable Sintered Metal Materials—Determination of Bubble Test Pore Size” (1977).

Received 2 February 2001
and accepted 26 February 2002