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Determining the pore Structure of Pore Structure of Individual Layers of Multi-Layered Ceramic Composites

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Abstract

Pore structures of ceramics materials are normally determined by porosimetry or flow porometry in which the flow occurs parallel to the thickness of the sample. Both of these techniques are incapable of determining the pore structure of individual layers of multi-layered composites. A novel technology based on flow porometry has been developed to measure the pore structure of individual layers. The technology is described and the pore structures of two layers of a composite ceramic filtration medium determined by this technology are presented**.**

Introduction

Multi-layered ceramics and functionally graded ceramic materials with gradually changing pore structure are being increasingly used for high technology applications. The effectiveness of such materials depends upon the pore structure of individual layers. Currently available techniques are incapable of providing the information. Porometry measures the pore volume and pore volume distribution of the entire composite. Moreover, in many of the composite filters one of the layers is very thin and the low pore volume associated with this layer is not detectable by porosimetry. Flow porometry measures pore size along the thickness direction of the material. A new technology based on the principles of flow porometry has been developed to measure pore structure of individual layers of a composite. In this communication, the new technology has been discussed and the analysis of results obtained with a two-layered ceramic composite has been presented.

Theoretical Background

For testing of a sample, its pores are filled spontaneously with a wetting liquid for which the liquid/sample surface free energy is less than the gas/sample surface free energy. Pressure of a non-reacting gas is slowly increased on one side of the sample so as to displace the liquid from the pores and increase gas flow through the sample. When the wetting liquid is displaced from the pore, the gas/sample interfacial area increases at the expense of the liquid/sample area and the free energy of the system increases. Gas can displace the liquid, only when the work done by the gas is equal to the increase in surface free energy. Equating the two energy terms [1], the differential pressure, p required for displacement of a low surface tension wetting liquid at a location in a pore is given by [2]:

$$p = \gamma (dS / dV) \qquad (1)$$

where γ is the surface tension of the wetting liquid, dS and dV are the increases in the gas/sample surface area and the volume of gas in the pore respectively. Diameter of a pore at any location along the length of the pore is defined as the diameter, D of a cylindrical opening such that (dS/dV) of the pore at the location is equal to that of the opening. For a cylindrical opening, (dS/dV) is $(4/D)$. Hence, Equation 1 reduces to:

$$D = 4 \gamma / p \qquad (2)$$

It follows from Equation 2 that pressure required to empty a pore is the smallest for the largest pore. Consequently, gas flow rate, which is zero at the beginning, starts at the pressure required to empty the largest pore and increases with increasing pressure because the smaller pores are emptied.

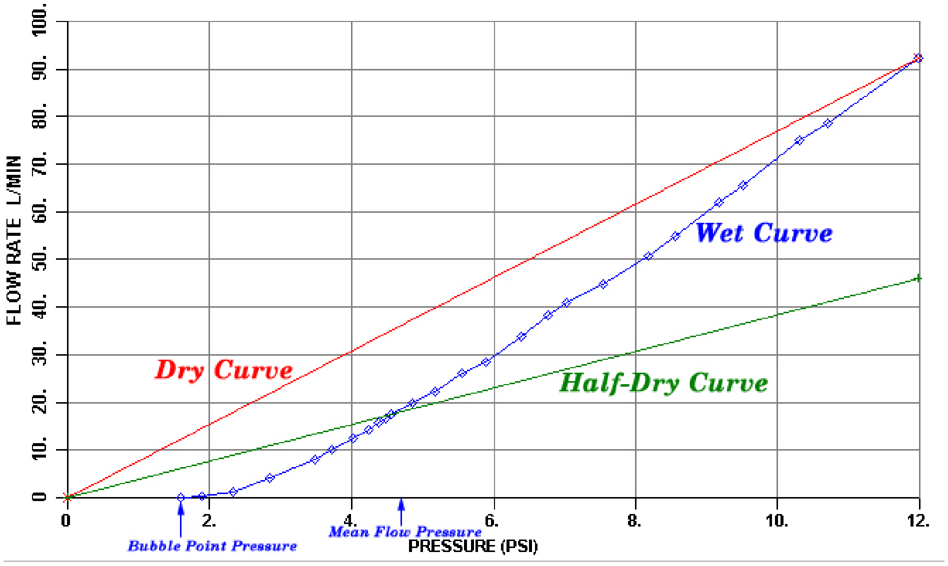

Figure 1. Flow rate of gas through dry and wet samples as functions of differential gas pressure

Typical results of tests carried out with dry and wet samples are shown in Figure 1. The figure also shows a half-dry curve that is calculated from the dry curve to yield half of the flow rate through the dry sample at any pressure. The indicated bubble point pressure is the pressure at which the largest pore is emptied, and the flow starts. The pressure at which the half-dry and wet curves intersect is indicated as the mean flow pressure. All of these data are used to determine the pore characteristics.

The Technology

The sketch of the two layered composite used in this study is outlined in Figure 2. Layer 1 is thin and has small pores. The layer 2 is thick and has large pores. Gas pressure required to empty pores in such a material filled with a wetting liquid is determined by pore size. The pore diameter normally varies along the length of a pore (Figure 3). Hence, the pressure required to displace the liquid (Equation 2) varies with location along the length of the pore and is a maximum at the most constricted part of the pore (Figure 3). When the pressure is equal to this maximum pressure, the pore becomes completely empty, gas flows through the pore and the presence of the pore is detected by flow porometry. Thus, flow porometry measures the diameter of the constricted part of the pore.

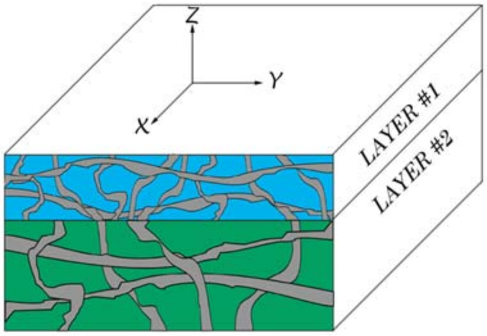

Figure 2 Sketch of the two-layer composite

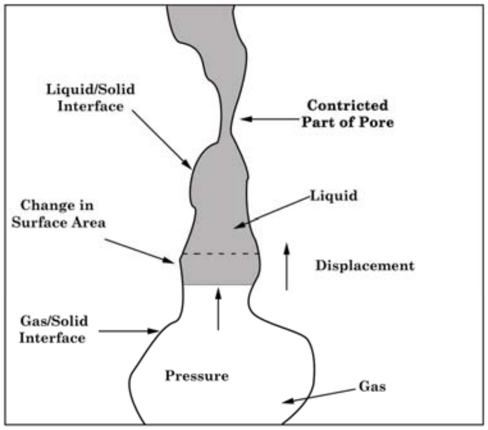

Figure 3 Pore showing variation of pore size along its length and the constricted pore size.

This basic principle is utilized to determine the pore structures of the two layers of the ceramic composite (Figure 3). The pores are filled with a wetting liquid and gas pressure under layer 2 is increased. If gas is allowed to flow in the z-direction, flow porometry measures the size of the constricted parts of pores along the z-direction. Because the pores in the two layers are in series, the small pores present in layer 1 act as constricted parts of z-direction pores. Therefore, the layer 1 pores are measured. On the other hand, if gas is allowed to flow in the x-y plane, gas will tend to flow simultaneously in pores of both layers, which are in parallel. Flow porometry will first detect the large pores in layer 2. At higher pressures, the pore pores of layer 1 will be detected. Thus, pore structures of both layers can be separately determined.

Figure 4 shows the arrangement for flow in the z-direction and Figure 5 shows the arrangement for flow along the x-y directions. Figure 6 shows the PMI flow porometer used in this study. This instrument, with state-of-the-art components, many innovative designs features and complete automation is capable of giving highly accurate and reproducible data [2].

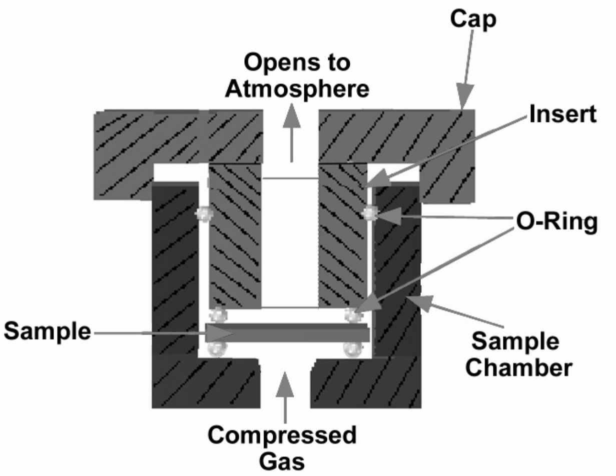

Figure 4 Arrangement for flow along the z-direction

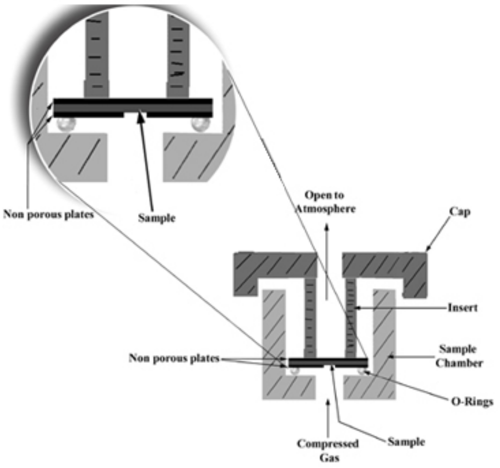

Figure 5 Arrangement for flow along the x-y directions

Figure 6 Capillary Flow Porometer

Results and Discussion

Pore structure of layer 1

Layer 1 had smaller pores. In order to find its pore structure, a sample saturated with silwick (γ = 20.1 dynes/cm) was placed between two o-rings in the sample chamber (Figure 4) and pressure of air under layer 2 was slowly increased. The air flowed only along the z-direction and escaped to the atmosphere because the o-rings prevented air from flowing in the x & y directions. The flow rates are shown in Figure 7. The largest pore diameter was calculated from the bubble point pressure. The mean flow pore diameter was calculated from the mean flow pressure. The mean flow pore diameter showed that half of the flow through the sample is through pores larger than the mean flow pore diameter. The pore diameters are listed in Table 1.

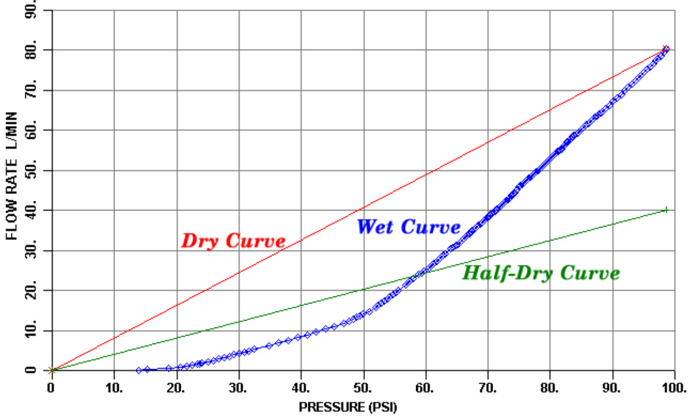

Figure 7 Flow rates for flow along the z-direction

The pore size distribution function, f is defined as:

$$f = - d\,[100\times(F_w / F_d)] / d\,D \qquad (3)$$

where F_w & F_d are flow rates through wet and dry samples respectively at the same differential pressure. The leading negative sign on the right hand side of the equation is due to the fact that (F_w / F_d) increases with decrease in pore diameter. The pore distribution is presented in Figure 8. The area under the curve in any size range gives the percentage flow in that range.

$$[100\times(F_w / F_d)]_{D2} - [100\times(F_w / F_d)]_{D1} = - {}_{D2}\int^{D2} f \; d\,D \qquad (4)$$

The amount of flow is determined by pore diameter and pore size. The pore distribution suggests that most of the pores are in the range of about 0.7 – 0.1 microns.

Table 1 Pore diameters

Layer	Diameter, microns	
	The largest pore	The mean flow pore
Layer 1	0.597	0.142
Layer 2	28.166	4.455

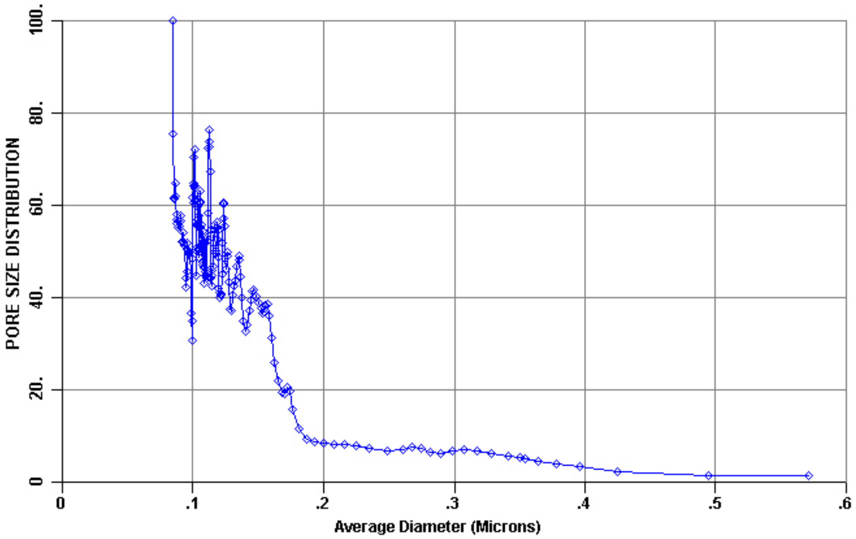

Figure 8 Pore size distribution in layer 1.

Pore structure of layer 2

Layer 2 had large pores. In order to analyze the pore structure, the sample was soaked in silwick, sandwiched between two non-porous plates and loaded in the sample chamber (Figure 5). A small central hole in the bottom plate (next to layer 2) allowed entry of air to the sample. Air could not escape in the z-direction because of the non-porous top plate, but could escape to the atmosphere by flowing in the x & y directions in the sample.

The flow rates through wet and dry samples are shown in Figure 1. The largest pore diameter and the mean flow diameter are listed in Table 1. As expected the pore diameters in layer 2 are much larger than those in layer 1.

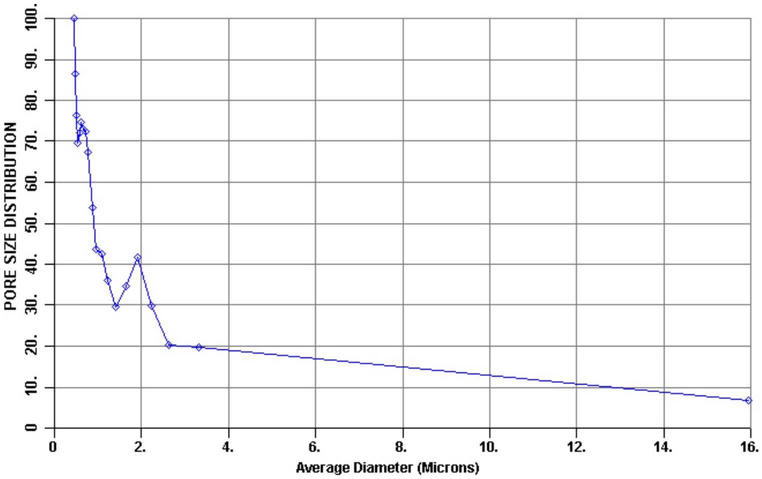

Figure 9 Pore distribution for flow in x & y directions

The pore distribution for flow through x & y directions are shown in Figure 9. When air pressure is increased, the large radial pores in layer 2 open up at low pressures. The group of large pores detected in the pore size range of about 0.5 to 4 microns is in layer 2. Had the pressure been increased to a high enough value, the small radial pores in layer 1 would have been detected. Thus, it was possible to measure both groups of pores in the two layers.

Mercury Porosimetry

The composite was also examined by mercury intrusion porosimetry. The results simply showed the pore volume of layer 2. No indication of the pore volume of layer 1 was obtained

Conclusions

(1) A novel technique based on flow porometry has been developed to determine the pore structures of individual layers of multi-layered ceramic composites.
(2) The principles of the technique and the technology have been described.
(3) A two-layered ceramic composite was examined by this technique.
(4) The largest pore diameter, the mean flow pore diameter and the pore size distribution of each layer were determined.
(5) Porosimetry could not measure any property of layer 1.

References

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2. Vibhor Gupta and A. K. Jena, Advances in Filtration and Separation Technology, Volume 13b, 1999,pp.833-844.