INFLUENCE OF STARCH CONTENT ON MICROSTRUCTURE OF POROUS YTTRIA - STABILIZED ZIRCONIA TAPES

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ABSTRACT

Porous yttria stabilized zirconia (YSZ) substrates with volume fractions of porosity ranging from 28.9 to 53 volume % were developed using starch as a fugitive additive. Concentrated aqueous YSZ slips with different amounts of starch and an acrylic latex binder were prepared. The influence of the volume fraction of starch on the final microstructure was investigated by FE-SEM. The porosities were above those predicted for all the starch contents examined. Two kinds of pores were observed in the sintered tapes: large pores created by the starch particles with lengths between 15 and 80 μm and smaller pores in the matrix with lengths between 0.6 and 3.8 μm. The SEM image of a tape with 17.6 vol.% starch showed isolated pores; the individual pores started to interact with increasing starch concentration to 37.8 vol.% and an open structure interconnecting the coarse pores was being gradually established. The higher interconnection between pores resulted in larger

cavities. The pores in the matrix reduced the sinterability of the YSZ leading to the retention of closed porosity in the sintered tapes.

Keywords: Porous ZrO_2 ceramic; thin films; Microstructure.

1. INTRODUCTION

Porous ceramics have a number of important applications in devices that include filters, gas burners, bioceramics, fuel-cell electrodes and membrane reactors, etc. [1-3]. In particular, copper-based ceramic-metallic (cermet) tapes are used for anodes in solid oxide fuel cells (SOFC) [4]. The synthesis of a porous YSZ matrix is the first step in the fabrication of the cermet . The Cu-YSZ cermet is then prepared by impregnating soluble salts of copper into the porous YSZ structure, after the YSZ has been sintered [4]. As the cermet anode should be 30 vol. % metal to ensure electronic conductivity, and should still remain highly porous to allow diffusion of fuel to the electrolyte interface, very high initial porosity (~ 40 vol. %) is desirable for the YSZ substrate before the addition of soluble salts of copper.

The objective of this work was to develop a porous YSZ matrix by tape-casting. One method to produce porous YSZ tapes is tape casting of YSZ with pore-forming agents. A carbon-based pyrolyzable pore former is mixed with the YSZ powder in the slurry preparation stage. The pore former is eliminated by combustion during the calcination at high temperature, leaving stable voids that are not removed during the subsequent sintering procedure [5]. A material is obtained after sintering with porosity corresponding to the original amount, shape and size of the starch particles. This method of introducing porosity offers a direct control over the porous characteristics of the final ceramic. In addition, it may be possible to form open pore networks because of the potential percolation of these pyrolyzable particles in the green body [5]. Starch is one of the more frequently used pore-forming agents; due to its chemical composition is easily burnt out during firing without residues in the final ceramic body [6]. It has also been shown that the morphology and the size of the pores are particular to the type of starch used to create the porosity [7].

The tape-casting process for porous ceramics involves the preparation of a concentrated YSZ suspension with the addition of a pore-forming agent, a binder and a plasticizer [8]. Aqueous-based tape casting offers several advantages due to the

low-cost, non toxic nature of the fluid vehicle. The development of such formulations has been a subject of recent research [9-11]. Kristoffersen et al. [10] evaluated different types of organic binders for aqueous tape casting of alumina. They found that latex binders yielded the highest solids loading suspensions, while still maintaining the appropriate rheological behavior. These emulsions have useful and unique characteristics such as internal plasticization and controllable crosslinking [11]. In the present work, we have developed an aqueous-based starch/YSZ/latex system for tape casting of porous ceramics.

The possibility of being able to control the microstructure of the porous YSZ tapes in terms of volume fraction of porosity, size and geometry of the pores is crucial in order to target particular properties for the final ceramic. Therefore, in this work, the influence of the volume fraction of starch on the final microstructure was investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

A commercial yttria doped YSZ powder (Y8Z01, Saint-Gobain, France) was used in this study. The mean particle diameter and the specific surface area were 0.53 μm and 8.26 m^2/g, respectively. Potato starch commercially available in Argentina was used as pore former agent. The starch granules exhibit a small degree of anisotropy with a median equivalent diameter of about 50 μm.

A commercial ammonium polyacrylate (NH$_4$PA) solution (Duramax D 3500, Rohm & Haas, Philadelphia PA) was used as a dispersant. The binder was an acrylic latex emulsion (Duramax B1000, Rohm & Haas, Philadelphia PA) with solids loading of 55 wt. %, an average particle size of 0.37 μm, and a glass transition temperature of -26 $^{\circ}$C.

2.2. Slip preparation

Concentrated aqueous YSZ suspensions with a solid loading of 77 wt. % were prepared by deagglomeration of the powder in distilled water with 0.3 wt. % NH$_4$PA (dry weight base of powder) using an ultrasonic bath. Different amounts of starch in the range of 13 to 33 wt% (dry weight base of YSZ powder) were added to the

stabilized YSZ slips, followed by ultrasonic treatment. Subsequent to this, 25 wt. % latex (dry weight basis with respect to (YSZ+ starch) powders) was added to the slurry, followed by additional stirring. The pH of the suspensions was adjusted to 9.0 with ammonia (25 wt. %).

2.3. Tape-casting

The slips were cast manually on a Mylar film using an extensor. The gap between the extensor and the film was adjusted to 0.4 mm. The cast tapes were subsequently dried in air at room temperature up to constant weight; afterwards, they were stripped from the film.

2.4. Burnout and sintering

The burn out of organic additives was achieved by slow heating (1 °C/min) up to 1000 °C. Then, the pre-calcined tapes were sintered at 1600 °C for 2 h, with a heating rate of 5 °C/min.

2.5. Characterization of green and sintered tapes

The tapes were weighted and measured geometrically to determine the green density. The bulk sintered density was calculated from the dimensions and weight of the sintered pieces. In order to calculate the relative green and sintered densities, density values of 6.05 and 1.45 g/cm^3 were used for YSZ and starch, respectively.

The open porosity and the pore size distribution of the sintered tapes were determined using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy). The microstructure of green and sintered samples were observed on fractured surfaces using a field emission scanning electron microscopy (FE-SEM) (Hitachi S-4700).

3. RESULTS AND DISCUSSION

Table 1 shows the compositions of YSZ tapes with different amounts of starch. We can define the following expressions:

V_S = volume of starch / bulk green volume, (V_T)   (1)

V_S = volume of starch / volume of starch+ volume of YSZ+ volume of latex+ volume of pores

F_{VS} = volume of starch / volume of solids   (2)

F_{VS} = volume of starch / volume of starch+ volume of YSZ+ volume of latex

F_{VZ} = volume of YSZ / volume of solids   (3)

F_{VL} = volume of latex / volume of solids   (4)

V_S indicates the volume of starch relative to the volume of the green tape; whereas, F_{VS} is the volume of starch with respect to the volume of solids.

Table1
Compositions of YSZ tapes with different amounts of starch

V_S (%)	F_{VS} (%)	F_{VZ} (%)	F_{VL} (%)	F_{VL}/F_{VZ}
0	0	42	58	1.38
17.6	19	31	50	1.61
28.4	30	25	45	1.82
37.8	40	19	41	2.16

The relative green density of the tapes with volume fraction of starch (V_S) between 0 and 37.8 % was 93-95 % of the theoretical density. The relative green density values were close to the theoretically predicted values. This indicates that some residual porosity, between 5 and 7 % remained in the tapes. A certain amount of porosity can be generated by air trapped in the suspension or by incomplete mixing of the powders during processing [5]. In addition, drying can also create non uniformly mixed powders in the green tape. Different settling behavior of the powder constituents and/or re agglomeration during solvent evaporation can also occur [5]. The volume fraction of starch in the green tape (V_S) was slightly lower than the volume fraction of added starch (F_{VS}), due to the presence of some residual porosity in the green body (Table 1).

Figure 1 shows the bulk YSZ packing density (δ_{YSZ}) in the matrix as a function of F_{VL}/F_{VZ} ratio. The bulk YSZ packing density in the matrix can be expressed by:

δ_{YSZ} = volume of YSZ / (V_T – volume of starch)   (5)

This parameter indicates the bulk packing density of the YSZ within the matrix, which is formed by the binder and pores, surrounding the starch particles.
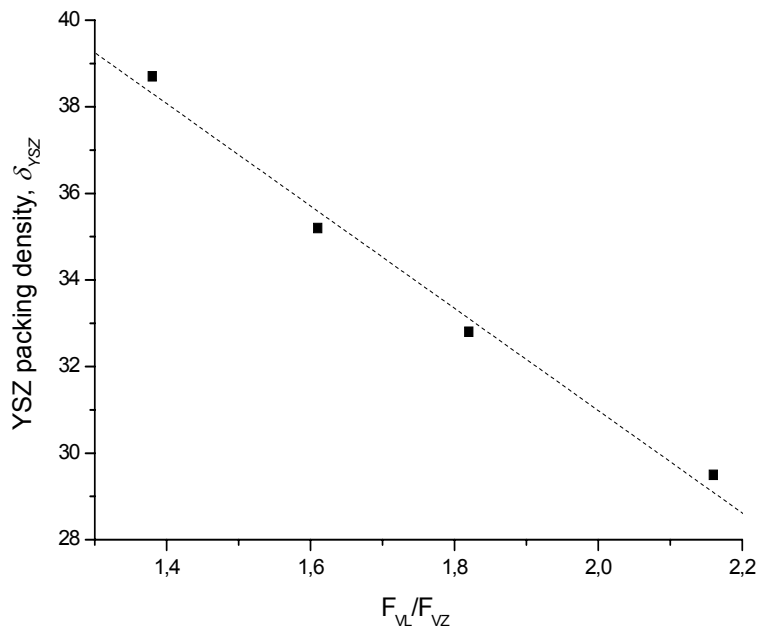
Fig.1: Bulk YSZ packing density in the matrix as a function of F_{VL}/F_{VZ} ratio.

As the amount of starch increased more latex was required to bind the particles, thereby increasing the F_{VL}/F_{VZ} ratio (Table 1). An approximately linear correlation between δ_{YSZ} and F_{VL}/F_{VZ} could be found; the added latex along with the starch decreased the bulk packing density of the YSZ powder within the matrix. This behavior has also been observed by our group in a previous study [12].

The relative sintered density of the tapes without starch sintered at 1600 °C was 90.3 % of the theoretical density. Thus, the YSZ tapes did not achieve full densification at 1600 °C. This observation was also noted for the tapes prepared with starch sintered at 1600 °C. Figure 2 shows a SEM image of a tape with 17.6 vol. % starch sintered at 1600 °C. The microstructure consisted of large pores created by the starch particles with length between 15 and 80 μm and smaller pores in the matrix with length between 0.6 and 3.8 μm. Thus, some closed porosity remained in the YSZ matrix of the sintered tapes.
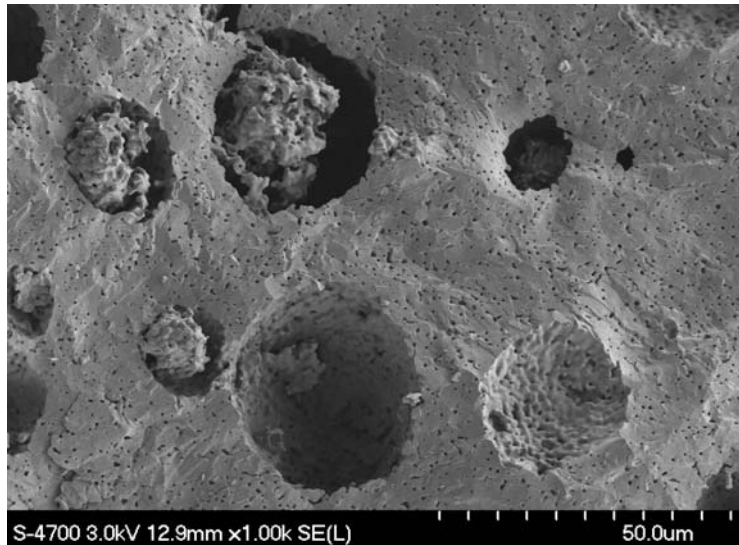
Figure 2: SEM micrograph of a tape with 17.6 vol. % starch sintered at 1600 °C.

Figure 3 shows the total bulk porosity of the tapes sintered at 1600 °C versus the volume fraction of starch in the green tape; the 1:1 relationship between the bulk porosity and the amount of starch is shown. This relationship assumed that a full densification of the YSZ matrix occurred and consequently the remaining porosity corresponds to the volume fraction of starch originally added.
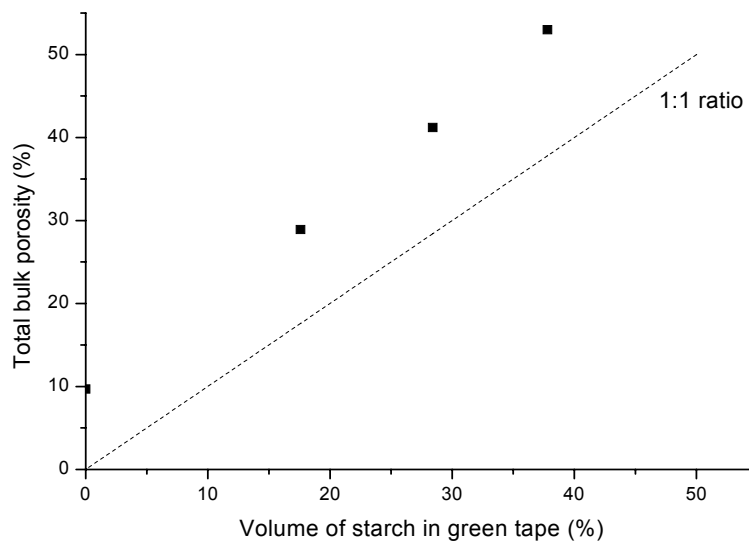

Figure 3: Total bulk porosity of tapes sintered at 1600 °C versus the volume fraction of starch in the green tape.

Deviations from the 1:1relationship could be seen, the porosities were above the predicted amount for all starch contents. Therefore, the higher porosity observed with respect to the amount of added starch was due to an incomplete densification of the YSZ matrix during sintering (Fig. 2).

Figure 4 shows the matrix of the tapes with 0 and 37.8 vol. % starch sintered at 1600°C.
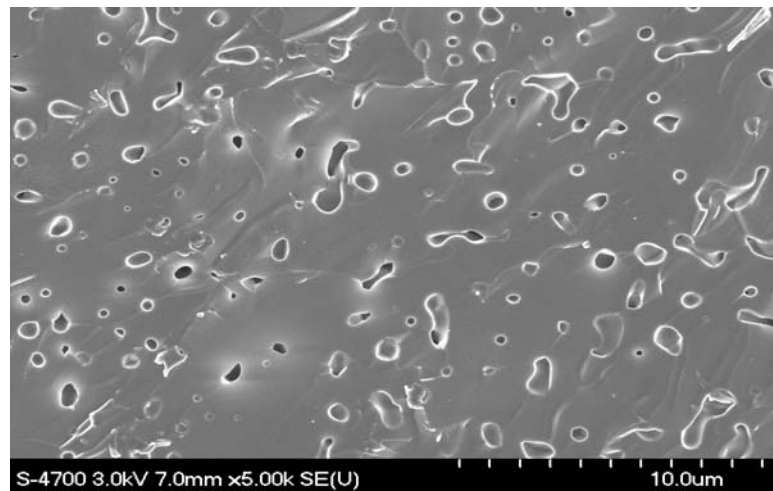
a
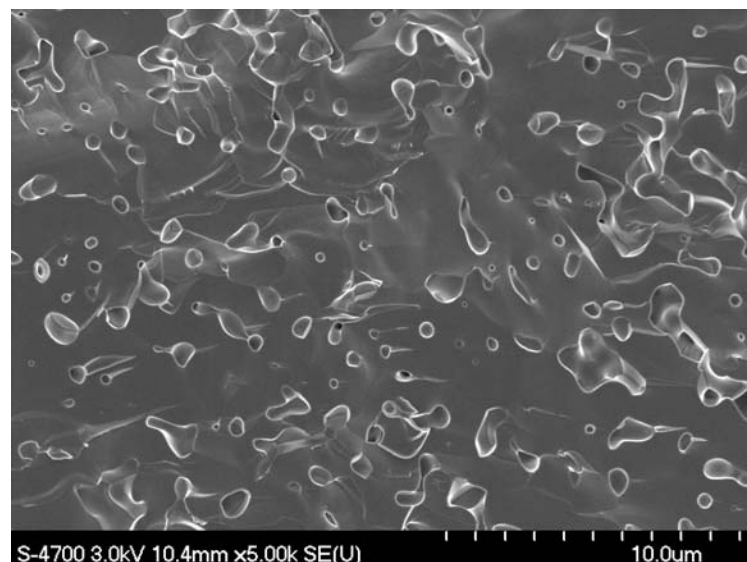
b

Fig. 4: The matrix microstructure of tapes sintered at 1600 °C with different volume fractions of starch: (a) 0, (b) 37.8 %.

The micrographs show rounded and elongated pores with length between 0.6 and 3.8 μm.

The coalescence of the latex particles during drying and the pore coalescence during sintering might contribute to the enlargement of the pores in the matrix. The onset of the latex coalescence is expected to occur during the drying of the cast-tapes when the volume fraction of latex particles approaches 0.6, its maximum solids loading [13]. The latex coalescence resulted in an increase in the particle size of the latex, thereby increasing the pore size left by the latex during burnout. The pores could also coalesce during sintering so that the pore size increased. The greater the pore size, the lower the driving force for sintering and shrinkage. The enlargement of the pores leads to a decreased sintering rate. Therefore, the large pores in the matrix reduced the sinterability of the YSZ leading to retained closed porosity in the sintered tapes. As a consequence, the porosities were above those predicted for all the starch contents.

Larger deviations from the predicted porosity as more starch was added were observed in Figure 3. An increase in the matrix porosity with increasing volume fraction of starch in the green tape was found in Fig. 4. The higher F_{VL}/F_{VZ} ratio for the tapes with increasing added starch decreased the YSZ packing density within the matrix, thereby increasing the matrix porosity after sintering at 1600 °C. Consequently, the larger deviations from the predicted porosity as more starch was added were attributed to the reduction in the YSZ packing density.

If the total bulk porosity of the tapes sintered at 1600 °C is plotted against V_S + P_0 (F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}) (Figure 5), the 1:1 relationship is followed. P_0 is the total porosity of the tapes without starch and the factor F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0} is the F_{VL}/F_{VZ} ratio of the green tapes with starch with respect to that of the tapes without starch. The term P_0 (F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}) represents the additional porosity produced by the latex volume added with respect to the YSZ which increased as more starch was added. Clearly, the total porosity of the tapes followed that predicted based on the volume fraction of starch in the green tape plus the additional porosity created by the adjustments of the formulation (higher F_{VL}/F_{VZ} ratio with increasing added starch).
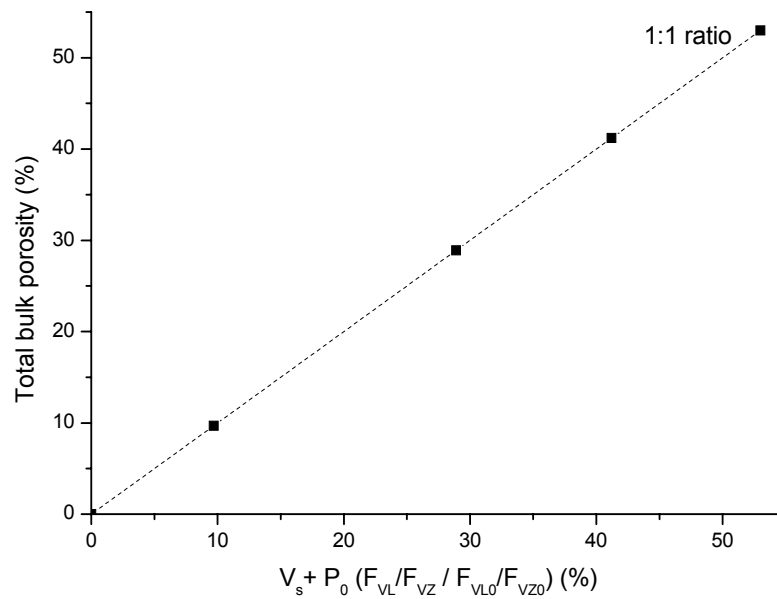
Fig. 5: Total bulk porosity of tapes sintered at 1600 °C versus $V_S + P_0$ (F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}).

Hg porosimetry was used to measure the smaller channels which corresponded to the connecting contacts voids between much larger pores created by the original starch particles. Figures 6 shows the differential pore size distribution curves of tapes with 0, 17.6, 28.4 and 37.8 vol. % starch, sintered at 1600 °C.

There was no open porosity for amounts of starch ≤ 17.6 vol. %; for starch contents ≥ 28.4 vol. % the open porosity corresponded to the connecting channels between the overlapping starch pores which resulted in a connected porous network in the sintered body. As the volume fraction of starch increased from 17.6 to 37.8 vol. %, there was a gradual increase in the volume and size of the connecting channels between pores, and consequently in the openness of the pore structure.

The most frequent channel radius at 1600 °C were 1.29 μm for 28.4 vol. % starch and 1.82-2.75 μm for 37.8 vol. % starch.
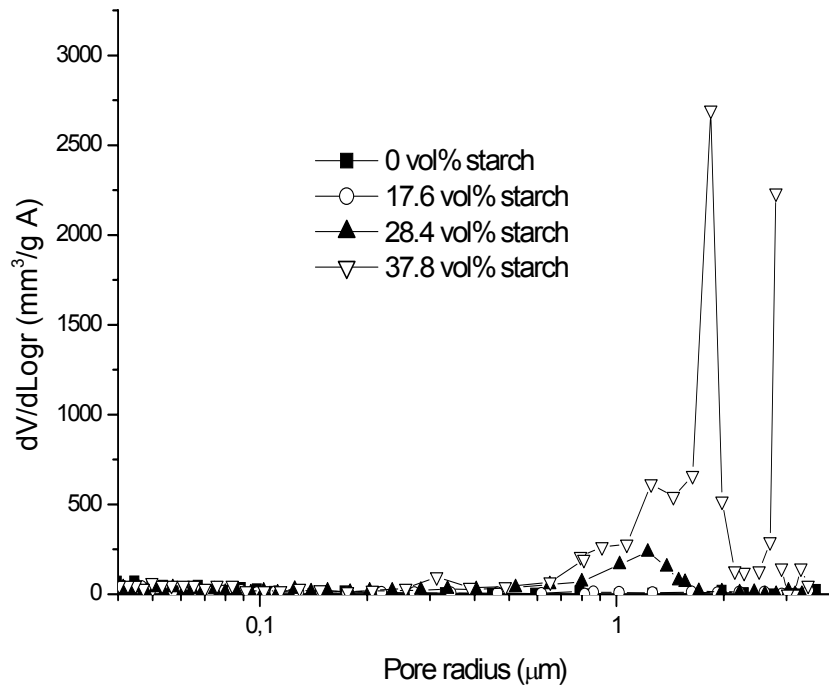
Fig. 6: Pore size distribution curves of tapes sintered at 1600 °C with different volume fractions of starch: (a) 0 %, (b) 17.6 %, (c) 28.4 %, (d) 37.8 %.

4. CONCLUSIONS

Porous YSZ tapes with volume fraction of porosity from 28.9 to 53% were developed using starch as a pore-forming agent.

Two kinds of pores were observed in the sintered tapes: large pores created by the starch particles with lengths between 15 and 80 μm and smaller pores in the matrix with lengths between 0.6 and 3.8 μm. The coalescence of the latex particles during the drying of the cast-tapes and the pore coalescence during sintering, might contribute to the enlargement of the pores in the matrix, reducing the sinterability of the YSZ and leading to closed porosity in the sintered tapes. Consequently, the porosities were above those predicted for all the starch contents examined.

The larger deviations from the predicted porosity as more starch was added were attributed to the reduction in the YSZ packing density within the matrix.

At 1600 °C, there was no open porosity for amounts of starch ≤ 17.6 vol. %; for starch contents ≥ 28.4 vol. % the open porosity corresponded to the connecting channels between the overlapping starch pores which resulted in a connected

porous network in the sintered body. As the volume fraction of starch increased from 17.6 to 37.8 vol. %, there was a gradual increase in the volume and size of the connecting channels between pores, and consequently in the openness of the pore structure.

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