Porous Ceramics Manufacture – Properties – Applications

Porous ceramics offer a broad range of characteristics that enable them to be used in a wide variety of applications. By selecting a suitable base material for the intended use, and then adjusting the overall porosity, pore size distribution and pore shape, they can be tailored to suit a diverse range of applications. This generally requires close consultation between the ceramics manufacturer and the customer or user.

Manufacture of porous ceramics

A number of different processing routes exist for the manufacture of porous ceramics depending on the application requirements and the specific material:

- Use of sacrificial templates
- Utilisation of gap grading
- Modified sintering process/partial sintering
- Casting of scaffolds
- Conversion methods.

In the following we will elaborate on the first three methods, as only these are of importance for the applications described here.

Casting of scaffold materials, for example from plastic foams [1], is employed commercially e.g. in the manufacture of casting filters. Conversion methods are based, for example, on the ceramisation of prepyrolised wood structures, paper structures etc. with metallic silicon to form SiC and are currently only produced in research quantities.

Depending on requirements, it is also possible to combine various methods to further fine-tune the characteristics of the porous ceramics [2].

Sacrificial templates materials (sometimes also referred to as pore-forming agents) are incorporated into the ceramic matrix and removed during thermal treatment [3–5]. These may consist of residue-free (or at least low residue) combustible solid materials such as plastic granulates, wood flour, artificial fibers, polystyrene beads, cellulose derivatives, etc. or air or other gases (foam ceramics) [6–7]. In the latter process, the gases are introduced into the liquid phase of the material (suspension, slurry) and the material is then solidified, thereby entrapping the gases.

The size and shape of the placeholder determines the shape and size of the pores. Depending on the forming method, it is also possible to align elongated pore-forming agents in a preferential direction (e.g. in the direction of extrusion in extrusion process, or transverse to the direction of compaction in pressing process). This can be used to produce anisotropic material properties. When removing the placeholder in a thermal process, special environmental protection measures (e.g. thermal post-combustion) often need to be taken.

A further option for producing porous ceramics is the use of targeted particle size distributions. Ceramic raw materials normally possess a relatively broad particle size distribution. This enables a high green density to be obtained, and also promotes dense sintering in the firing process. When a range of particle sizes is removed, or a narrow but relatively coarse mono-sized distribution is used, a lower packing density is obtained during forming process and pores remain between the particles (Fig. 1). The resultant pores between the particles are no longer collapsed during sintering because they are too large. The pore size can be directly controlled by adjusting the particle size distribution [8].

When sintering ceramic materials, the materials follow a specific densification curve. In the course of the firing process, some initial bridges are first formed between the particles (sintering necks), then increased densification and shrinkage of the material occurs until the final density is reached.

Shrinkage during the sintering process occurs through the elimination of the pores by transport processes and particle growth (Fig. 2) [9]. Interrupting the sintering process in an early phase also provides a means of achieving a well-defined porosity [2, 10]. It is important to ensure that the sintering process is interrupted during a phase in which only a small amount of densification is occurring (region with a low shrinkage rate) otherwise the reproducibility of the produced porosity will be very low.

Keywords
porous ceramics, throttle element, ceramic wick, ceramic diaphragm, crushable ceramics

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Properties of porous ceramics

Porous ceramic materials consist of at least two phases: a ceramic (solid) phase, and the mostly gas-filled porous phase. The gas content of the pores usually adjusts itself to the environment as an exchange of gas with the environment is possible through pore channels. Closed pores can contain a gas composition that is independent of the environment. The ceramic (matrix) material can either be single phase or, as is often the case, multi-phase (e.g. one more crystalline phases and a glass phase).

When specifying the porosity, a distinction needs to be made between open (accessible from the outside) porosity and closed porosity. Open porosity can be further classified into open dead-end pores and open pore channels (Fig. 3).

Depending on the particular application, either a more open porosity (e.g. a filter element that needs to be permeable) or a closed porosity (e.g. a thermal insulator) may be desired. The sum of the open and closed porosity is referred to as the total porosity. If the fractional porosity of a material is relatively low, then the closed porosity will dominate; as the fractional porosity increases, the open porosity level increases. A literature review on the analysis of numerous materials (UN, porous metals, ZrO_2, graphite foam, MgO granulates, stainless steel and UO_2) has been carried out by Schulz [11].

Besides specifying the type and degree of porosity, it also important to describe the size distribution of pores when describing a porous material. The pore size distribution is usually measured by mercury penetration porosimetry. The pore size distribution of the closed porosity is not determinable using this method, but may occur, for example, by optical examination of a polished cross section.

Several properties of the matrix material are not influenced by porosity and are therefore also applicable to the porous material (e.g. coefficient of thermal expansion), however most properties are dependent on the total porosity and therefore need to be redetermined for the porous material (e.g. mechanical strength, electrical properties, etc.).

Applications

The fields of application and specific forms of porous ceramics are wide and varied. Applications such as gas and liquid filtration, catalyst supports, thermal insulators, kiln furniture, biomedical applications and lots more have been reported.

In the most recent issues of CERAMIC APPLICATIONS, there have been detailed reports on the application of porous ceramics in filtration [13] and ceramic honeycombs [14]. We will now report on several implemented projects in which porous ceramics played a decisive role. We will discuss the, at times, very complex requirements profile of these applications, and how these were fulfilled through the use of a porous ceramic.

Throttle element for a flashing light

The objective was to redevelop a porous ceramic throttle element to be employed in

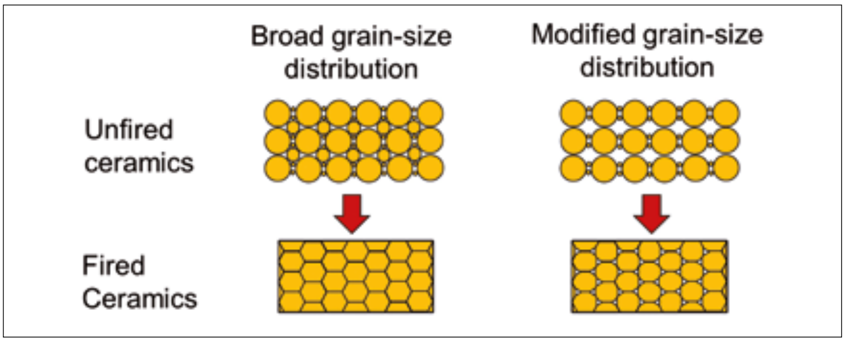

Fig. 1
Schematic of the sintering process with a modified particle size distribution. The customary way of producing dense ceramics is shown on the left; on the right is an example of how a targeted porosity can be produced by modifying the particle size distribution

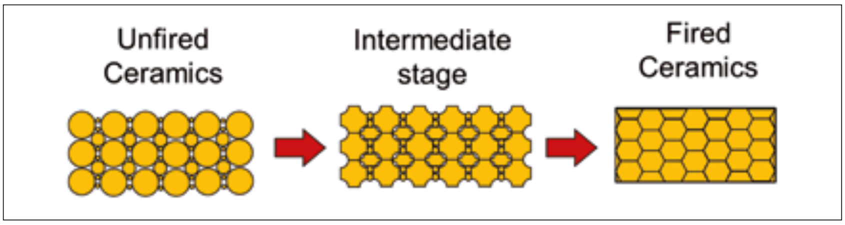

Fig. 2
Schematic of the sintering stages for ceramics. To produce porous ceramics, the sintering process is interrupted at a well-defined intermediate stage

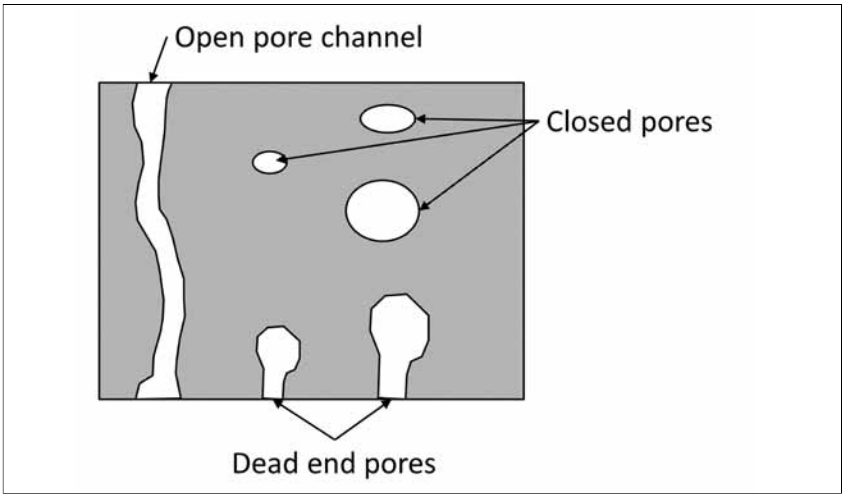

Fig. 3
Schematic of pore types

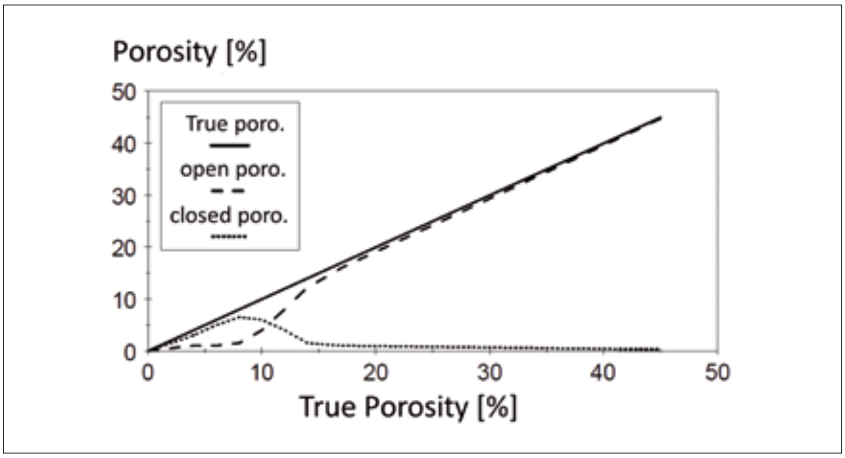

Fig. 4
Typical proportions of open and closed porosity in the total porosity [12]

a mercury relay of the company Siemens that is used to control the flash rate of a flashing light used at railway crossings. The aforementioned flasher relay is still employed in several legacy installations in Germany, but remains standard equipment in India because of its very robust, reliable construction and long service life (according to unconfirmed reports, such relays have been use for over 50 years). Furthermore, it can be used in wide temperature ranges (the solidification point of mercury is less than –35 °C, its boiling point is >350 °C) and it is also insect-proof – many plastics are eaten away and destroyed by aggressive insects. Since the mercury is incorporated into a closed system, there is no risk to health when handled correctly.

Fig. 5
Typical products made from porous ceramics

The complete relay unit is produced in a complex glass-blowing operation in which a heating element, switching contact and the porous ceramic are combined.

The principle of operation is as follows: When a voltage is applied, the heating element is switched on by means of a switching contact. This very rapidly heats the gas in gas compartment 1, thereby displacing the mercury column away from the switching contact 1. This switches off the heating element while simultaneously switching on the flashing light. The porous ceramic equalises the pressure between gas compartment 1 and gas compartment 2 therefore causing the mercury to slosh back. This switches the flashing light off again, and switches the heating element back on. This occurs in a cycle time of approx. 1 s. The cycle time can be set by adjusting the permeability of the porous ceramic. A video of a functioning flashing relay can be found on www.youtube.com on the Internet by searching for "RB 109".

The know-how for producing the required ceramic component no longer exists within the company, that developed the relay because production of this ceramic ceased in the 1970s, the technical specifications were lost during various company acquisitions, etc., and the persons with the technical expertise are no longer accessible to us. The company Hermetiko GmbH (Fürth/DE) has been manufacturing the flashing relay for some years now based on the old specifications. Up until 2011, all orders had been fulfilled using stocks of the ceramic from earlier production runs.

The glass construction of the relay places the following requirements on the ceramic:

- The CTE (coefficient of thermal expansion) of the ceramic must be tailored to the glass material otherwise cracks would form in the glass (CTE ceramic < CTE glass), leakage could arise between the ceramic and glass, or the ceramic could detach itself from the glass (CTE ceramic > CTE glass).
- The ceramic, while being fused into the glass, must not outgas otherwise gas bubbles could form at the ceramic-glass interface which would also result in leakage and not give a reproducible flash rate.
- The ceramic must possess an excellent TSR (thermal shock resistance) because the ceramic pin is fused through the short-term application of a gas flame at a temperature of over 1000 °C.
- The ceramic disk must also be mechanically stable, which poses a significant challenge given the required high level of porosity.
- As per the requirements, the permeability must be adjustable in order to precisely control the flash rate.
- The length of the pin, which is required to have a diameter of 8–12 mm, must be at least 75 % of the diameter otherwise the pin could tilt out of alignment while being fused into the glass tube. A solution involving the use of thin, porous ceramic discs was therefore rejected in the very early stages. The diameter itself is less critical, but needs to be in the range of 8 to 12 mm.

After a number of iterative steps involving the production, installation and testing of a prototype ceramic at the company Hermetiko GmbH, a functioning ceramic, which was successfully employed in a series production flashing relay, was able to be delivered through a collaborative effort spanning more than a year.

A solution was found by using magnesium silicate based pins, which exhibit an extremely high open porosity of >50 %. The

Fig. 6
Mercury relay for railway flashing lights, porous ceramic circled (total heights: approx 200 mm)

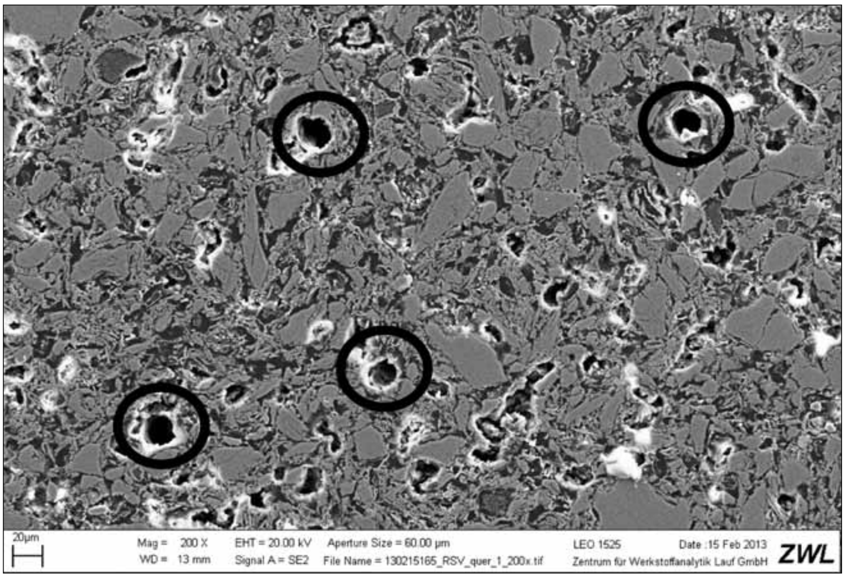

Fig. 7
Polished section of a porous ceramic used as a throttle element in a mercury relay. The lengthwise pores with a diameter of approx. 20 µm have been marked

mechanical strength of these pins was also significantly higher than the previously used material.

The high porosity was able to be achieved through a combination of a partial sintering process and sacrificial templates, plus the targeted incorporation in the lengthwise direction of pores with a diameter of approx. 20 µm and a length of several millimeters (Fig. 7).

Wick for vaporisation of liquids

Wicks are used in technical processes and household applications (insecticides or air fresheners) for the controlled, continuous vaporisation of liquids. Ceramic wicks are preferred in a number of applications, whereby the wick extends into a reservoir of liquid, and is filled with the liquid as it is drawn up through the action of capillary forces. The liquid rises in the wick and is vaporised at the surface of the wick, this vaporisation often being supported by a small heating element. These wicks need to fulfil the following requirements:

- Generally round rods with an external diameter typically in the range of 5–8 mm and a length between 60 and 80 mm. This is the typical size of wicks that are used in bottles that provide a 30 to 60 day supply of liquid.
- An adjustable capillarity/vaporisation rate depending on the liquid being vaporised. The wick material must be compatible in each case with the carrier liquid used.
- Chemically inert to the liquids used, as the media being vaporised are often organic.
- No blockage as a result of vaporisation residues during long-term operation (up to several weeks).
- Mechanically stable (3-point bending strength >8 MPa) so the wick can be securely mounted but will not be damaged if accidentally touched by the consumer during use of the vaporiser.

This requirements profile was met by using the materials Rapor P0,3 and Rapor P1 (a magnesium silicate based material); for specialised applications, it is also possible to use Rapor P20 (aluminium oxide based). By varying the sintering process, it is possible to adjust the capillarity of Rapor P0,3 and Rapor P1. Capillarity is defined as the time required to fully saturate with water a standard wick that has been inserted 20 mm into the water. This is proportional to the vaporisation rate of a water-based liquid, e.g. an insecticide. The mechanical strength of >15 MPa (typical value 20 MPa) is more than adequate for this application (min. 8 MPa is required).

Diaphragms for analytic applications

When manufacturing so-called single-rod electrodes cells for the measurement of the pH value or redox potential of liquids, porous ceramic diaphragms, which can close the electrical circuit between the reference electrode and the fluid being measured, are required. In this application, ceramics compete with ground diaphragms, spongy platinum and porous plastics.

The requirements on the ceramic diaphragms are as follows:

- The diameter of the rod needs to be in the range of 1,0 to 1,2 mm.
- The length of the rod is not particularly relevant, because only a short section is fused into the glass and the remainder is broken off for use in the next electrode.
- The porosity and pore size must be adjusted so that a small but defined discharge of electrolyte through the diaphragm to the outside can occur, otherwise the composition of the electrolyte could change and lead to incorrect measurements.
- The ceramic, while being fused into the glass, must not outgas otherwise gas bubbles could form at the ceramic-glass interface, which would cause a too high leakage.
- The CTE of the ceramic rod must be kept within certain limits so that a variety of glass types can be processed. At the same time, there must be no formation of cracks in the glass or inadequate adhesion of the ceramic within the glass (see above).
- A good chemical resistance of the material allows it be used with strong acids and bases.
- Because the ceramic is subjected to a gas flame for a brief time when fusing it into the glass, it must also have a good TSR, however this property is less critical in this application than the flashing relay application described in the previous section because of the small diameter.

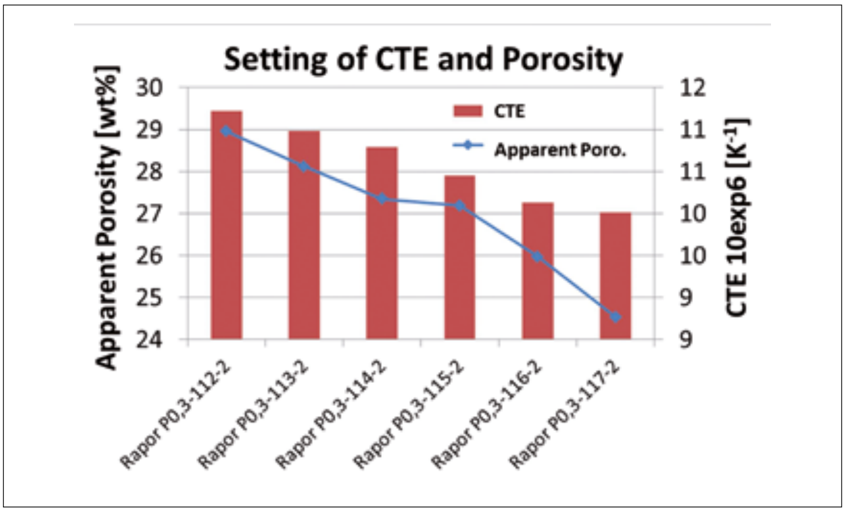

Fig. 8
Adjustment of the coefficient of thermal expansion and the resultant open porosity characteristics of Rapor P0,3

Fig. 9
Typical crushable ceramics based on magnesium oxide, smallest external diameter in the image is 1,7 mm, the largest tubes have an external diameter of 25 mm

Two possible materials are suitable for the application described above:

1) Rapor P0,3: A magnesium silicate based material that is well suited for applications that do not place too high requirements on the chemical resistance of the diaphragm. This material also allows the CTE to be adjusted within a certain range (Fig. 8).

Due to the nature of this material system, adjustment of the CTE also leads to a change in the porosity. These changes do not matter in these applications, however. The CTE is adjusted by heat treatment.

2) The second option is to use a Y-FSZ based material. This material has a much better chemical resistance, but the disadvantage that it has a fixed CTE value; the total porosity can however be adjusted within the range of 20 % to 45 %. The material can be tailored to the particular application by adjusting the porosity.

Porous crushable ceramics for heating elements and sheathed thermocouples

To produce crushable ceramics, as used in the manufacture of sheathed thermocouples and high-density heating elements, porous ceramics based on magnesium oxide or steatite C230 are specifically employed. These ceramics are prepared so as have such a low mechanical strength that the ceramic components can be broken down again into a powder during the compression process used by the manufacturer of the heating elements or sheathed thermocouples. Typical geometries for these crushable ceramics are shown in Fig. 9.

To manufacture heating elements, so-called mandrels are first produced by an extrusion process dried and fired. An ultrafine filament is then wound around the outside of the mandrel, the geometry (pitch) of which can be used to produce an application-specific power distribution along the length of the heating element. Thicker wires are fed through the holes in the centre to serve as external connecting elements, and these are connected with the ultrafine filament. The mandrels are then centred in a metallic sheath tube by means of spacers (shown at front centre in Fig. 9) or thin-walled casing tubes (shown at left in Fig. 9). The intermediate spaces are filled with free-flowing MgO powder. The external diameter of the metallic sheath tube is then reduced by 10 to 20 % by means of a hammering or swaging process. This reduces the ceramic components to their primary particle size, thereby firmly embedding the filament and connection wires within them. Thanks to the compact ceramic, a good electrical insulation is obtained between the filaments and the connection wires, as well as outwards to the metallic casing. At the same time, the high density of the material guarantees good thermal conduction to the outside. Other design variants are possible, but will not be discussed here for space reasons.

To manufacture sheathed thermocouples, wires made of the thermocouple materials are threaded through the holes of larger-sized MgO tubes (typical external diameter between 15 and 25 mm). A sheath tube of the desired material is slid over the top and the ends hermetically sealed. Compaction is then usually performed by means of a drawing process, similar to the manufacture of wire. The reduction in external diameter leads to an elongation of the material. In the first compaction step, the MgO tube is immediately reduced to a powder of the primary particle size, thereby establishing the required spacing between the thermocouples themselves, and to the casing. After one or two drawing steps, the casing must be softened again in an annealing process to eliminate the brittleness and hardening of the casing material resulting from the drawing operation.

The requirements on these ceramics are as follows:

- The diameter of the components ranges from 1,3 – 40 mm, whereby a wide variety of hole geometries (hole diameter, hole spacing) may be used. The length of the components range from 2 mm to max 1000 mm, typically max. 500 mm.
- The porosity must be adjusted so that the mechanical strength lies within a

specified, product-specific range. If the parts are too soft, they will break when the heating element or sheathed thermocouple is assembled by the manufacturer; if they are too hard, then compaction will be incomplete or inhomogeneous.
- The ceramic must be formulated so that it includes none of the "poisons" for heating wire materials and thermocouples.
- In the case of sheathed thermocouples, it must be ensured that they contain no oversized particles which can disrupt the thermocouple strands or the sheath.

To fulfil this requirements profile, two possible solutions with regard to the choice of material are available: For heating elements with application temperatures up to approx. 500 °C and with low or medium power requirements, the porous Steatite C230 material offers a good solution. For higher temperatures and power densities, the preferred material is MgO based on fused magnesia, and for sheathed thermocouples magnesium oxide, or very seldom for specialised applications aluminium oxide or spinel, are used. The adjustment to the required mechanical strength range occurs during the firing process, where unavoidable batch-wise variations in the raw materials can be compensated for. Through careful selection of the raw materials and analyses, it is possible to ensure that the materials contain no harmful impurities. Oversized particles can be reliably removed by performing multiple sieving steps.

Summary

Porous ceramics can be produced from a range of material groups, some of which have been discussed here by way of several practical examples. In addition to the materials described above, Rauschert also produces a number of other porous ceramics: magnesium silicate, Y-FSZ, Al_2O_3, TiO_2, MgO, mullite, cordierite, etc.

Precise adjustment of the material characteristics, for example open porosity, pore size distribution and pore shape, and sometimes CTE as well, often requires close consultation with the customer or user. The base material must be tailored to the specific requirements of the application. Many remarkable solutions to customer requirements can thereby be achieved.

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