Cost-Efficient Directly Foamed Ceramics for High-Temperature Thermal Insulation

Highly insulating materials are key factors for energy-efficient thermal processes. While fibre-based insulation panels provide excellent thermal insulation, they suffer from poor mechanical strength and abrasion resistance. Furthermore, high prices due to high production costs and the release of fibre dust are disadvantages in their practical application. Lightweight refractory bricks, on the contrary, are inexpensive and mechanically stable, but exhibit a high thermal mass and high thermal conductivity. Highly porous directly foamed ceramics, also referred to as ceramic foams, are an alternative capable of filling the gap between fibre-based insulation panels and lightweight refractory bricks in thermal insulation. The Fraunhofer Center HTL/DE has developed a direct foaming process to produce cost-efficient ceramic foams for high-temperature insulation.

Introduction

Thermal insulation materials are used to spatially and thermally separate the chambers of furnaces from the surrounding. They have to fulfil several requirements in their practical application. First of all, they have to be thermally, chemically and dimensionally stable up to the maximum service temperature. Furthermore, insulation materials need to provide minimal thermal conductivity for good thermal insulation and low space requirements. In addition, the mechanical and thermo-mechanical stability has to be high enough to bear the load of structural elements positioned above them. In case of batch furnaces, thermal cycling resistance is also essential for a long service life. Due to the considerable volume of thermal insulation in furnaces, the prices of the respective elements also have to be kept low to be competitive [1].

Keywords
ceramic foams, thermal insulation, direct foaming

In order to keep the overall costs for insulation low, furnace walls, especially in large furnaces, are often built up from several layers of insulating materials. They are assorted along the temperature gradient from the furnace chamber to the ambiance in terms of maximum service temperature, thermal conductivity, mechanical stability and price [2].

Generally, a low thermal conductivity can be achieved by the implementation of pores into a host material. In case of ceramics, several manufacturing routes have been developed, which include partial sintering, additive manufacturing, hollow bead sintering, sacrificial templating, replica foams and direct foaming.

Partial sintering of coarse-grained masses, e.g., is an easy and cost-effective way to achieve refractory products with lowered densities, but leads to a limited specific strength and limited maximum porosity. The sintering of ceramic hollow beads is an alternative, which leads to parts with a generally high compressive strength, yet limited maximum porosity and high prices for raw materials. It is mostly used in lightweight engineering and for kiln furniture. Via Additive Manufacturing (AM), near-net-shape porous parts with tailored pore structures can be fabricated with a high material efficiency. AM is therefore particularly suited for the production of individualized and load-oriented bone scaffold structures made of more expensive raw material, so the process-related high costs for the production of the parts are mitigated [3].

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For a more straightforward production of highly porous ceramics, three main fabrication routes can be determined (Fig. 1). The so-called replica method (RM) is based on coherent natural or synthetic cellular structures such as polyurethane foams as sacrificial bodies. The pores of the cellular structures are infiltrated with ceramic slurries or preceramic compounds, and the cellular structures are then burnt out before sintering, which relieves the final replica foam. In using this technique, extremely high porosities up to 92 vol.-% with predominantly large open pores are accessible, which is why this process technique has been established for the production of ceramic filter elements or catalyst carriers [4]. Likewise, the burning of a large volume of hydrocarbons in order to get a small volume fraction of ceramic material leads to long burning times and a high carbon dioxide footprint, and the foam struts are prone to break during pyrolysis [5].

The sacrificial templating method (STM) uses placeholders such as natural or synthetic hydrocarbons, liquids, or metals during moulding, which are dispersed in the ceramic raw material and relieved via pyrolysis, evaporation, sublimation or leaching before the actual sintering process. In using this technique, a broad range of porosities from 20–90 vol.-% is accessible. Furthermore, the pore shape and the size distribution can be tailored in a broad range by the choice of suitable sacrificial raw materials. Also closed pores are accessible. The drawback of the STM technique lies in the removal step of the placeholders: the burning of large volumes of hydrocarbons, e.g., leads to high gas pressures inside the green parts, so long burnout times have to be chosen to avoid crack formation. Furthermore, the elimination of organic placeholders is likely to cause cracks and results in a large carbon dioxide footprint. When using liquids or metals as templates, the extensive sublimation or leaching steps cause high costs per volume and low throughput [4].

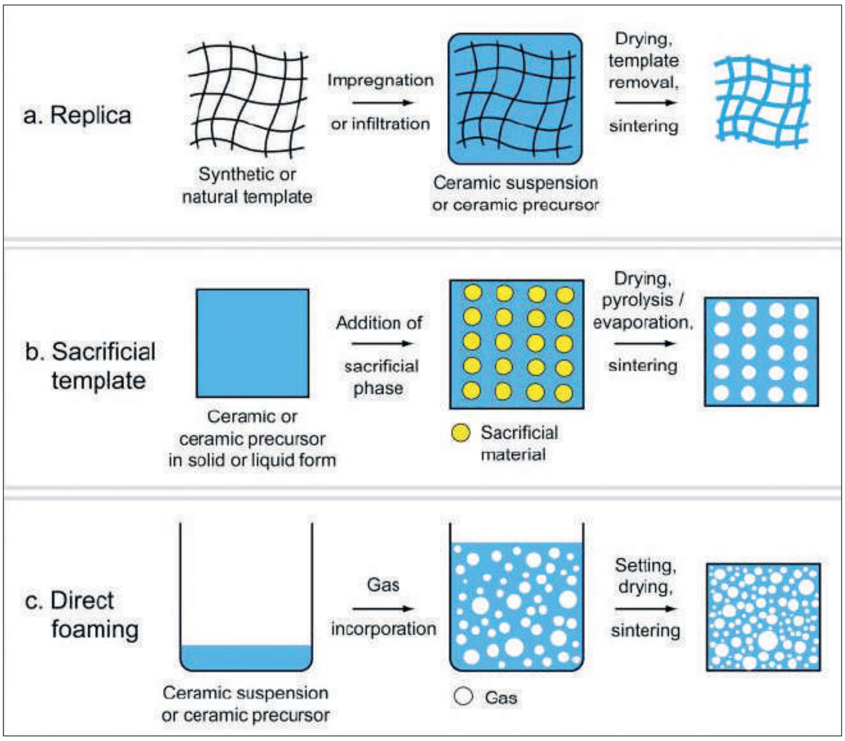

Fig. 1
Schemes of the three principal routes to obtain highly porous ceramics [4]

Direct foaming

When thinking about the production of highly porous ceramic bodies, why not use gases or even surrounding air as a main raw material? Direct foaming processes use the formation of gases in or the incorporation of gases into ceramic precursor materials to establish porosities up to +95 vol.-% in the most material efficient way [4]. In direct foaming, in turn, three main routes can be outlined. Chemical direct foaming uses gas formation during chemical reactions in order to produce gas bubbles in ceramic slurries or preceramic polymers. Physical direct foaming utilises the incorporation of gas into the liquid phase via gas pressure and bubble formation upon pressure drop. In mechanical direct foaming, gas bubbles of the surrounding air are injected into mainly water-based slurries via turbulent stirring. Therefore, suitable surfactants have to be chosen in order to provide for an adequate foamability and short-term foam stabilisation.

Concerning all of these approaches, long-term foam stabilisation against bubble coalescence, Ostwald ripening and drainage is essential to yield stable ceramic foams with high porosities and a homogeneous pore structure. Therefore, mostly gellants are used to freeze the foam structure, before foam aging and collapse can occur. Up to now, a diverse range of gellants has been used to stabilise ceramic foams. Among them are thermosetting polymers or polysaccharides, thermosetting or pH-setting herbal or animal proteins, monomers conducting radical polymerization, hydraulically setting cements, and sol-gel precursors. Directly foamed ceramics have recently been commercialized [6, 7].

The production of cost-efficient highly porous ceramics requires inexpensive raw materials and processes. Therefore, mechanical direct foaming of water-based ceramic slurries is an interesting approach. At the Fraunhofer Center HTL, a direct foaming process of this type has been developed and patented [8]. It aims at competitive highly porous ceramics for the use as durable insulation material, especially for temperatures >1400 °C [9].

Experimental

The practical realisation of the manufacturing process is depicted in Fig. 2. At first, a slurry is prepared, which contains deionized water, ceramic particles, associative thickeners and a plant-based gelling agent. Associative thickeners are commonly used in the food and cosmetics industry in order to thicken water-based formulations like creams and pastes in a

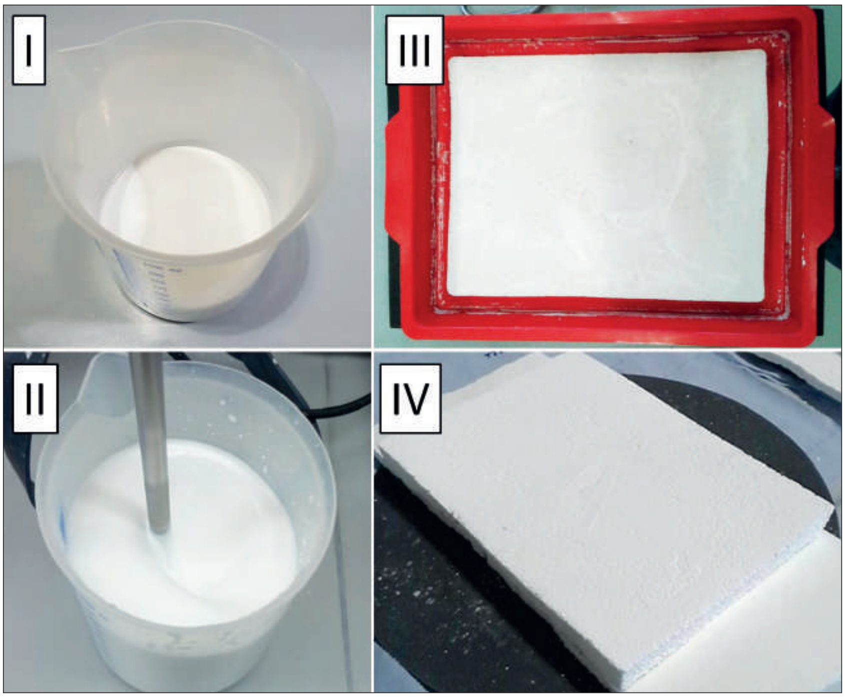

Fig. 2
Mechanical direct foaming process chain: I: viscoelastic slurry; II: mechanical frothing with a stirrer; III: green panel after moulding, gelling and drying; IV: alumina panel fabricated via mechanical direct foaming, porosity about 70 vol.-%, 290 mm × 210 mm × 20 mm

way that the desired viscoelastic properties can be obtained. In the case of direct foaming, they both act as surfactant and provide for the required viscoelastic properties, so foamable slurries can be obtained. As gelling agents, inexpensive and environmentally friendly herbal proteins like gluten or modified polysaccharides are used.

The slurries are subsequently mechanically frothed, e.g. using a dissolver, turbine stirrer or even a milk frother. Due to the simplicity of the equipment required, production of foams in a broad range of small to large batches is possible. After frothing, the slurry foams are transferred to a mold. Depending on the viscoelastic properties adjusted, the slurry foams can be stiff to moderately flowable. Using shape moulds and flowable slurry foams, near-net shape fabrication becomes possible depending on the geometrical details of the parts. The filled moulds are then placed in an oven to be thermally treated for gelation and drying at temperatures <100 °C. During this process, the viscoelastic foams turn to elastic green foams, so the foam aging is impeded and the foam structure frozen. The foams or parts of the foams can also be deformed plastically in order to yield areas with increased density and mechanical strength.

Following the drying step, the foams are thermally treated for debinding and sintering. Due to the large open porosity, the pyrolytic gases can escape easily, so debinding can be conducted in an efficient way. As the specific weight and thermal mass of the debindered foams are comparatively low, sintering can also be performed without any major restrictions. With the developed process technology, arbitrary ceramic powder raw materials can be processed, as demonstrated on cordierite, alumina and mullite (Fig. 3). Nevertheless, the process is not restricted to these materials and can be applied to any inorganic powder materials. Also thin sheets down to 4 mm height can be fabricated (Fig. 4).

Properties of the directly foamed ceramics

Depending on the viscoelastic properties of the slurry, the solid content and the

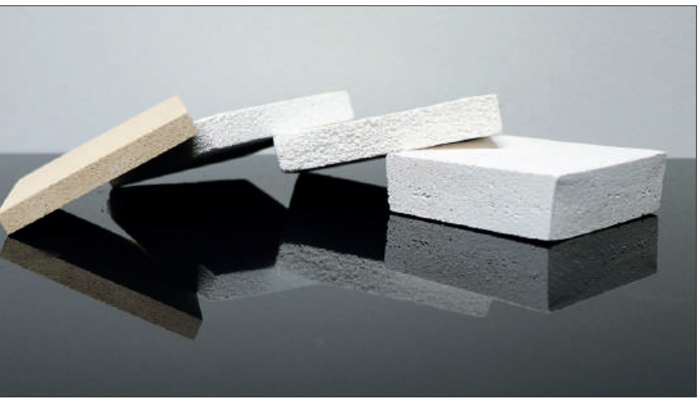

Fig. 3
Directly foamed ceramic blocks (ca. 90 mm x 90 mm x 10 – 30 mm) made of cordierite (l.), and alumina (three parts at the right) at porosities ranging from 80 vol.-% (2nd f. l.) to 65 vol.-% (r.)

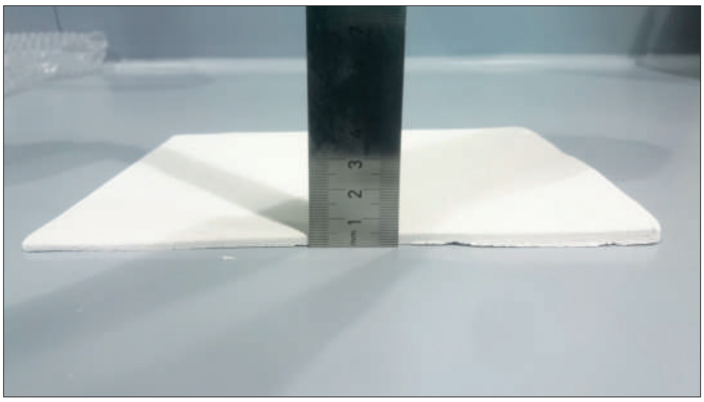

Fig. 4
Sintered alumina foam sheet with a thickness of about 4 mm, length about 290 mm, width about 210 mm

conditions during thermal treatment for gelation and drying, foams with open porosities ranging from 55–85 vol.-% can be obtained. The resulting pores are interconnected and vary in a range of 20–400 µm (Fig. 5). Porosity, pore size and pore size distribution can be controlled via slurry rheology. Fig. 6 shows some values for the porosity, cold crushing strength and permanent linear shrinkage after thermal treatment for ceramic foams developed at the Fraunhofer Center HTL, in comparison to commercial foams, refractory bricks and vacuum-based panels.
Ceramic foams can reach the mechanical strength of refractory bricks, while having a considerably higher porosity. Accordingly, low thermal conductivity values especially at high temperatures can be achieved depending on the raw materials used, and the actual porosity and the pore structure obtained (Fig. 7). The values of the thermal conductivity for ceramic foams are only factor two to three times as high as for high-temperature vacuum insulation panels, while the foams exhibit a significantly higher compressive strength. Due to the use of inexpensive raw materials, the simple process and the fast thermal treatment, production costs in the range of refractory bricks can be reached [10].

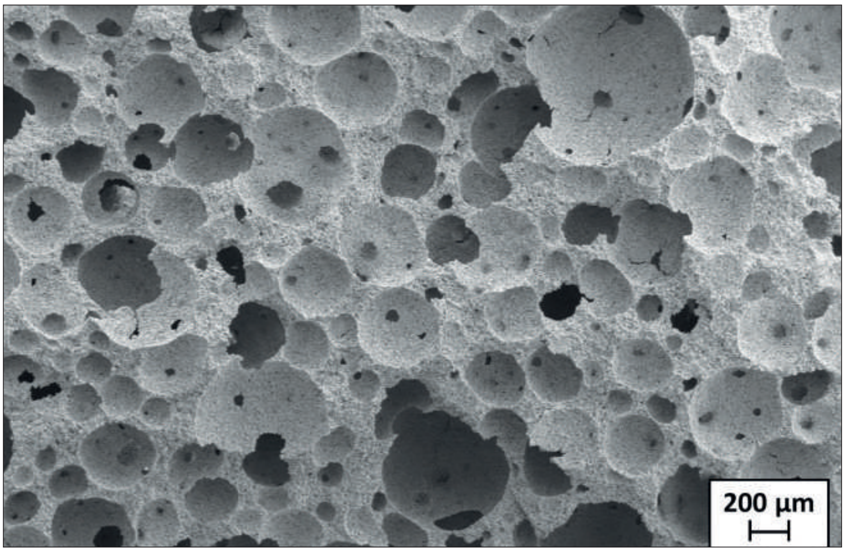

Fig. 5
SEM-picture of the microstructure of a mullite foam with a porosity of about 70 vol.-% (magnification 25×, working distance 15 mm, EHT 10 kV, secondary electron detector)

Conclusions
Direct foaming of water-based slurries is a cost-efficient and easy approach to fabricate highly porous ceramics for insulation applications. The porosities as well as thermal and mechanical properties achieved are in between refractory fibre bricks and fibre-based insulation panels. The raw materials, the process

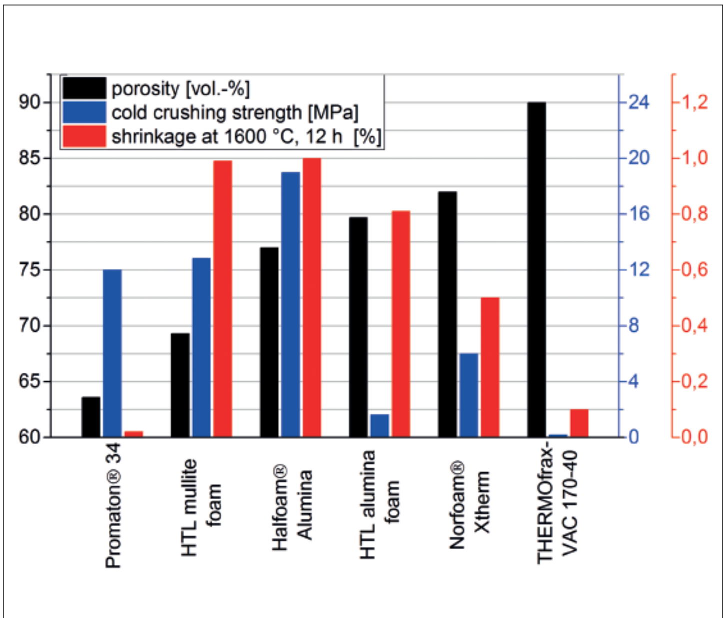

Fig. 6
Porosity, cold crushing strength and permanent linear shrinkage after 12 h at 1600 °C of directly foamed ceramics developed at the Fraunhofer Center HTL in comparison to commercial high-temperature lightweight firebrick (Promaton® 34), commercial alumina foam (Halfoam® Alumina), commercial mullite-zirconia foam (Norfoam® Xtherm) and fibre-based vacuum-formed sheet (THERMOfrax-VAC 170-40)

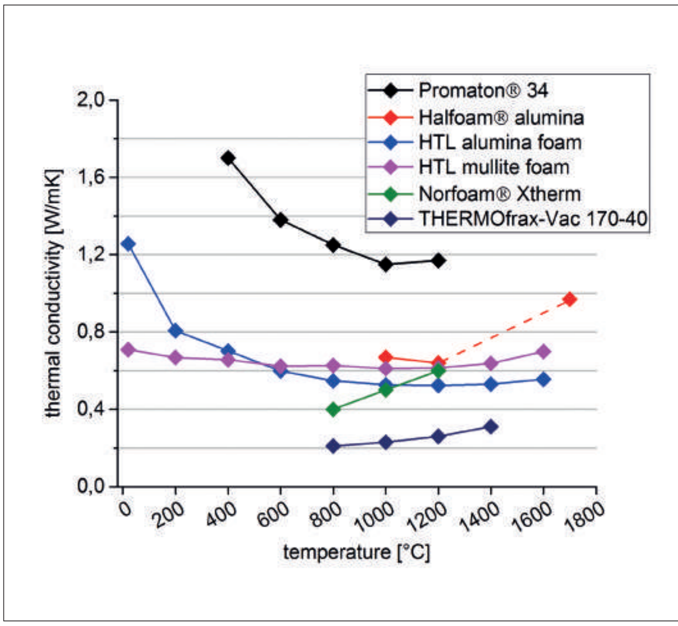

Fig. 7
Comparison of the thermal conductivity values of the samples mentioned in Fig. 6

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Key topics: additive manufacturing • electro-ceramics • polymer derived ceramics • sourcing raw materials • market growth • R&D processes • thermal management • end-user applications itself and the required equipment are inexpensive, and the thermal processes can be conducted efficiently. Therefore, the overall production costs are estimated to be in the range of lightweight refractory bricks, but an order of magnitude lower than fibre-based insulation panels and also well below polycrystalline fibre wools. The foams can be shaped via moulding and plastic deformation during gelling. Therefore, they can be used for near-net-shaped, inexpensive yet stable and effective insulation components. Considering the broad range of materials and achievable properties and shapes, also other applications like lightweight kiln furniture, hot gas filtration or bio-scaffolds can possibly be served.

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