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Fabrication of highly porous glass filters using capillary suspension processing

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ABSTRACT

We present a novel, capillary suspension based processing route for sintered glass filters with porosities $\geqslant$50% at average pore sizes between 1 and 50 μm. This new kind of glass filters exhibits narrow pore size distribution and uniform pore structure. Pores are exceptionally smooth and round. Accordingly, permeability and mechanical strength of these filters excel that of similarly processed ceramic and commercial glass filters significantly.

Mechanical strength at a given porosity is much higher than that of commercial glass filters and reaches values similar to that of ceramic filters with distinctly higher matrix strength. Absolute values are well predicted by the Gibson & Ashby model $\sigma_c/\sigma_{f,0} = B_0(1-\varepsilon)^z$ with $B_0 = 0.8$. Liquid permeability varies with pore size according to Darcy's law but absolute values are clearly higher than that for ceramic filters at given pore size as expected from the smoother pore structure. Gas permeability is especially high at pore sizes <10 μm and exceeds that of ceramic and commercial glass filters significantly. Moreover, this results in a weaker than quadratic pore size dependence. This is presumably due to slip effects occurring especially in small pores and narrow necks of the novel glass filters.

1. Introduction

In the field of microfiltration the increasing number of applications at high temperatures, covering greater pH ranges and including chemically more aggressive media results in a need of inorganic filter media [1,2]. Inorganic filters become increasingly popular for large volume solid–liquid separation processes such as in waste water recycling or drinking water treatment [3,4]. Furthermore, inorganic filters or membranes find their applications in industrial hot gas cleaning processes [5] or for the purification of liquid metals [6]. As polymeric materials cannot withstand the extreme conditions regarding temperature, chemical and mechanical resistance occurring in the exemplified applications, there is a strong trend to ceramic and glass filter media for industrial purposes. Their outstanding chemical resistance is a key advantage of glass filters. Since the chemical resistance is dependent of the composition of the glass itself, it is obvious to choose an appropriate glass for the respective scope of application. Borosilicate glasses are examples for high resistant glasses which are applied for nearly all kinds of laboratory glassware. Their hydrolytic, acidic and basic resistance is high even at elevated temperatures. Furthermore, these properties are for some kinds of glasses combined with a high thermal shock resistance. Therefore, potential fields of application of the glass filters presented here range from beverage industries [3,7], over gas filtration purposes to applications in laboratory equipment. The smooth pore structure and the narrow pore size distribution are promising indicators for a good fouling resistance, good back flushing behavior and a narrow cut-off range. As the manufacturing of fine granulated and fractured glass powders can be expensive, but the sintering process is performed at temperatures well below sintering temperatures of ceramic materials, the specific costs of these glass filters range in between polymer and ceramic filters.

Typical established filters made of glass are either fiber filters, leached glass membranes, porous silica glass prepared via the sol–gel process or sintered glasses. Nearly all subsequently summarized manufacturing methods not only apply to glass but also for manufacturing metallic [8,9] or ceramic filters [10,11], while sol–gel processes are exclusively for non-metallic materials and leaching is a typical manufacturing method for microporous glass membranes. For fiber filters in pad or blanket form the thin glass fibers are bound together by their intrinsic properties or by impregnation of the sheets with suitable resins or adhesives. Typical pore sizes are in the range of 1 up to 50 μm [12,13]. Via phase separation and leaching of alkali glasses porous membranes

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with pore sizes in the range of 1–1000 nm are achieved. After forming the glass part a heat treatment in the temperature range between 500 and 700 °C initiates a phase separation. Two different phases arise from the homogeneous glass, while an alkali-rich phase can be leached out by mineral acids, alcohols or water at moderate temperature (RT up to 100 °C). Since the other phase is almost pure silica, a porous glass with silica content of about 96% is achieved [14]. Glasses with pore sizes below 1 μm also result from the sol gel-process. Here a silicate suspension gets gelled in a chemical reaction, dried and sintered in a following heat treatment [15]. The processes introduced above are most common but porous glass filters can also be produced via sintering processes. This provides better control of pore size, porosity, pore shape and uniformity. Sintered filters own a higher mechanical strength and a higher heat resistance than the cheaper glass fiber filters, where organic binders often limit the operating temperature [16]. The sintering of glass powder via the sacrificial templating method where additional fillers (e.g. salts, organic materials) are added as pore forming agents is limited to pore sizes between 20 and 200 μm [14]. A further technique for manufacturing porous sintering materials is the replica technique. Natural or synthetic organic templates are filled with a suspension of glass particles. After drying of the infiltrated templates all organic components get pyrolized in a debinding step, the following sintering step consolidates the replicated structure [14,17], and typically pore sizes >10 μm are achieved [10]. Enke et al. [14,17] reported about the combination of these two methods with the leaching technique. Glass monoliths with a hierarchical porosity and a bimodal pore size distribution can be manufactured. Furthermore, the partial sintering is a common manufacturing method for porous sintering materials. The final products exhibit a wide size range of open pores [10,18]. Various companies (e.g. DURAN Group GmbH, Heraeus Quarzglas GmbH & Co. KG) produce porous glass frits and filters in the pore size range between 1 and 300 μm, while in products with pore sizes <60 μm porosities are well below 40%.

The processing route based on capillary suspensions as presented here allows for manufacturing sintered filters with a porosity >50% and average pore sizes in a range of 1–50 μm. Porosity and pore sizes are the result of the controlled heterogenization of suspensions using capillary forces. The particle network structure of these so-called capillary suspensions can be preserved even in the sintered part. Ceramic capillary suspensions were already successfully applied as precursors for manufacturing porous ceramics [19,20].

Capillary suspensions, disperse systems consisting of a solid and two immiscible fluid phases, represent a distinct class of materials. Particles are essentially suspended in the major or so-called bulk fluid phase. The secondary fluid phase occupies only a small fraction of the liquid volume (<5 vol%), which is trapped in the capillary bridges formed at the particle contact points [21].

Adding an appropriate secondary liquid phase to a suspension changes the rheological behavior from fluid or weakly elastic to gel-like. In the pure suspension the particles are either well dispersed or they form already a sample-spanning fractal network due to dominating van-der-Waals attraction. Upon addition of the secondary fluid capillary bridges between particles are formed.

Since capillary suspensions based on glass and ceramic particles show such a strong and easy to control structure formation they can be used as precursor for highly porous sintering materials. The homogeneous sample spanning network can be preserved even during debinding and completely open-porous sintered parts are accessible. The manufacturing of macroporous ceramic sintered parts based on capillary suspensions [19] and their microstructure and mechanical strength in dependence of secondary phase content [20] have been described earlier. Now we discuss the processing of sintered glass filters manufactured with this new processing route. We demonstrate that the filters based on capillary suspensions and glass powder show significant advantages regarding permeability compared to ceramic and commercial glass filters. Moreover, the mechanical strength reaches similar values as ceramic filters at a given porosity.

2. Experimental

The experiments were carried out using a capillary suspension system based on glass with a composition similar to borosilicate glass in three different particle sizes as solid phase, paraffin oil as bulk fluid phase and an aqueous sucrose solution as the secondary fluid phase. With this material system we fabricated sintered parts for microstructural characterization, mechanical strength measurements and filtration tests.

2.1. Raw materials

Glass powders with compositions similar to borosilicate glasses (Technical Glass G018-361; SCHOTT AG, Mainz, Germany) with three different particle sizes and density $\rho = 2.75$ g/cm^3 were used. The particle size distribution as determined through Fraunhofer diffraction (Helos H0309; Sympatec GmbH, Clausthal-Zellerfeld, Germany) using in water dispersed particles in an ultrasonic wet dispersing unit (Quixel and Cuvette, Sympatec GmbH) for all three glass species is shown in Fig. 1. Obviously, Glass 2 exhibits a monomodal fairly narrow particle size distribution, whereas the other two powders show a broad slightly bimodal size distribution. The average volume based diameters are $x_{50,3} = 11.0$ μm (glass 1), $x_{50,3} = 1.1$ μm (glass 2) and $x_{50,3} = 0.6$ μm (glass 3). Scanning-electron-microscopy (SEM) micrographs (S-4500; Hitachi High-Technologies Europe GmbH, Krefeld, Germany) helped to get information about the particle morphology (Fig. 1). The bulk phase was paraffin oil (Carl Roth, Karlsruhe, Germany) with a Newtonian flow behavior and a dynamic viscosity $\eta(20\ °C) = 0.03$ Pa s. To prevent unwanted agglomeration in the pure suspensions of glass 3 the nonionic wetting agent Polysorbat 20 (Tween20; Carl Roth, Karlsruhe, Germany) with HLB = 16.7 was used. The secondary phase was a 1.853 M aqueous sucrose solution. The D(+)-sucrose (Carl Roth, Karlsruhe, Germany) was dissolved in distilled water at 20 °C. The solution shows a dynamic viscosity of $\eta(20\ °C) = 0.08$ Pa s.

2.2. Processing route

The main processing steps for manufacturing porous glasses based on capillary suspensions are summarized in the following flow sheet (Fig. 2). Pure suspensions were prepared by mixing the solid powder into the bulk phase with a high shear dissolver at a speed of 1200 rpm for 10 min. For a better homogenization the pure suspensions were then treated in a self-constructed ball mill for 24 h. Adding a small amount of surfactant (0.7 vol% of the bulk fluid phase) to suspensions consisting of glass 3 prevents unwanted agglomeration. The capillary network formation is induced by adding the secondary fluid phase to the pure suspension again using a high shear dissolver at a speed of 800 rpm for 5 min, followed by a period of 2 min with reduced stirring speed at 500 rpm. A final homogenization step in a ball mill with a rotation speed of 18 rpm and 25 mm balls for 24–48 h (depending on particle size) allows for the formation of homogeneous capillary suspensions without agglomerates. The solid content of the prepared capillary suspensions was between $\phi = 10$–20 vol%. Next to capillary suspensions consisting of one powder fraction, also mixtures consisting of glass 1 and glass 2 as well as glass 2 and glass 3 were used. Sintered parts with pore sizes in between those