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Short communication

Hierarchically structured glass monoliths based on polyurethane foams as template

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Abstract

Hierarchically porous glass foams were prepared via a combination of a replication technique and a phase separation of sodium borosilicate glasses. Open-pore polyurethane foams were impregnated with a slurry containing sodium borosilicate glass powder, binders, solvents and stabilizers. The composite was calcinated and sintered whereupon the organic polymer was decomposed and the monolith was compacted. A phase separation was initiated by an additional thermal treatment. The sodium-rich borate phase in the phase separated glass was removed with hydrochloric acid. Finally, the secondary silica species within the pores generated by the acid treatment were removed with sodium hydroxide solution. The monoliths were characterized by electron microscopy, nitrogen sorption, μ-CT and mercury porosimetry. Pore diameters – obtained from the template structure – were achieved in a range of 0.4–1.0 mm. The following phase separation and the coupled acid-alkaline leaching lead to an additional pore system within the glass framework.

Keywords: Phase separation; Porous glass foams; Hierarchical

1. Introduction

There are two big aims of natural science, nowadays. The one aim is the understanding of chemical, physical and biological processes. The other aim is the development of new processes and materials. Porous materials are since the early 20th century in the focus of research, because of their high application potential. Biological, physical and chemical processes often require materials with defined internal and external structure as well as defined pore sizes. Porous glasses, based on phase-separation in alkali borosilicate glasses are a good alternative to other commonly used porous materials. Due to their chemical and thermal resistance and the possible structural modifications, materials based on alkali borosilicate glass are usable in many processes such as heterogeneous catalysis and biotechnological applications. Porous glasses are prepared according to the VYCOR-process, which was developed in 1934 by Nordberg and Hood.[1] But due to the monomodal pore structure and potential limitations in diffusion, the numbers of applications is rather narrow. To increase this number of applications and the mass transport within the porous material, the insertion of an additional pore system in the meso- or macropore range will be advantageous. A possible way is the preparation of sintered glasses according to the filler principle.[2]

Two other innovative ways are the gas-related foaming and the replication method. The gas-related foaming can be conducted by an in situ gas evolution or by introducing an external gas into a glass suspension.[3] The gas-related foaming needs a long-term stabilization of the gas bubbles, which increases the bubble size during foaming. At a specific gas-bubble volume the lamellas tend to thin out, which leads to cracking of the walls and finally to an open-cell structure.[3]

Another approach is the replication method, which is more important, because of its industrial use. Thereby, an open-cell organic polymer foam is covered with a suspension,

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containing glass and different functional additives. In this impregnation step, thin layers of glass-suspension are deposited on the polymeric struts. After drying the polymer is burned out by thermal treatment and the resulting unstable calcinated structure is sintered.[4] The resulting product is a stable, macroporous open-cell glass foam, featuring hollow struts, due to the removal of the template. The foams are exact replications of the template. There are several ways to impregnate the template, for example Dip-coating, Drop-coating, as well as chemical vapor deposition (CVD).[5] The replication method is known since 1963 and was patented by Schwartzwalder.[6] The application of these open-cell foams was primarily limited to catalyst supports in automobiles. Nowadays open-cell foams are still used as catalyst support, but there are several other important applications. An interesting application of transparent, open-cell glass foams is the use as light thinning internals in photo-bio-reactors, where an algae solution is deposited in the pore structure, aerated and irradiated, to produce oxygen and biomass.[7]

In this paper we report for the first time the preparation of open-cell, hierarchically-structured glass foams. Those are obtained by replicating a macroporous polyurethane foam and inserting an additional pore system by a combination of sintering and phase separation of alkali borosilicate glass. The textural properties of the resulting materials were characterized by Hg-intrusion, N_2-adsorption, scanning electron microscopy (SEM) and μ-computer tomography (μ-CT).

2. Experimental procedure

2.1. Materials

An alkali borosilicate glass of the composition 1 wt% Al_2O_3, 7 wt% Na_2O, 30 wt% B_2O_3 and 62 wt% SiO_2 was used as starting material for the generation of the hierarchically structured glass foams. The initial glass was grounded and fractionated to particle sizes smaller than 32 μm. A cubic, open cell polyurethane foam with a cell density of 30 ppi (EHEIM Pickup, Deizisau) was used as template. The solvent for the soluble components was a mixture of 0.04 N hydrochloric acid and isopropyl alcohol (99.97% Fischer Scientific). Sodium chloride (>99.5%, Fluka) was used as a stabilizer during calcination and sintering. To obtain a strong adhesive strength and consequently an allover coating of the template surface, polyvinyl alcohol (PVA, MW = 88,000 g mol^{-1}, 88% Acros) was used as a binding agent.

2.2. Preparation

A general scheme for the preparation of glass foams with a bimodal pore system is shown in Fig. 1. The composition of the suspension for the impregnation is given in Table 1. The weighted amount of additives was mixed with the solvent under continuous stirring and heated under reflux, to obtain a clear solution. Afterwards the heater was removed and the solution was allowed to cool down under continuous stirring. After adding the glass, the mixture was stirred again, until a homogeneous slurry was obtained. At a constant rate shear of 200 s^{-1} at 298 K the viscosity of the slurry was 58 mPa s. Increasing the shear rate only led to small changes in the viscosity, concluding, that the slurry nearly shows Newtonian behavior.

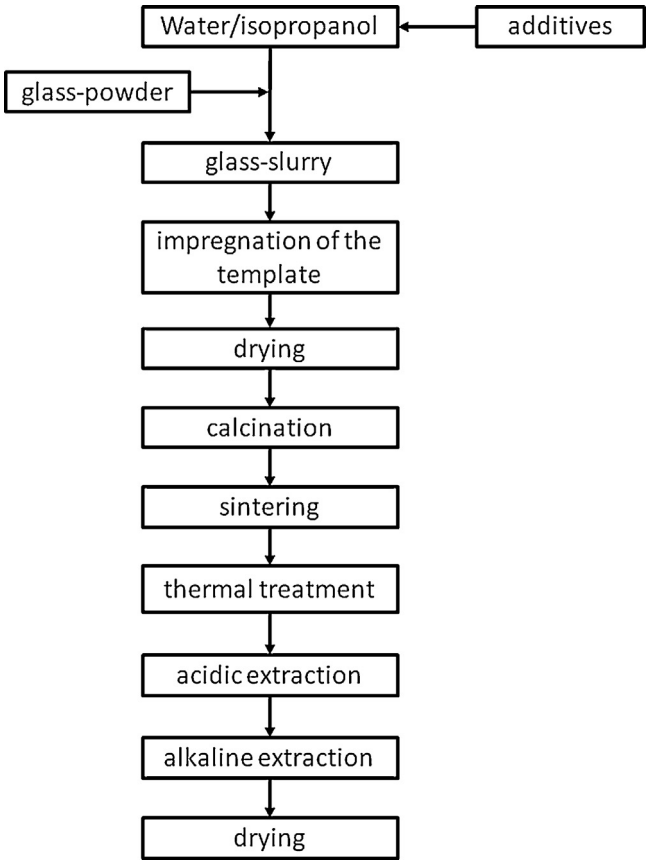

Fig. 1. General preparation scheme for hierarchically structured glass foams.

A polyurethane foam, of defined size (10 mm × 10 mm × 20 mm) was immersed into the slurry and compressed 20 times from each side. The excess slurry was removed and the remaining slurry was spread within the template by treating with pressurized air, followed by a drying step at room temperature for 24 h. The calcination was carried out at 573 K for 2 h followed by an additional treatment at 773 K for 4 h. The heating rate was 120 K h^{-1}. Then the calcinated bodies were sintered at 933 K for 30 min and afterwards allowed to cool down to room temperature (sample: GF-0; GF – glass foam).

The sintered glass monoliths were additionally thermally treated at 873 K for 24 h to initiate the phase separation. The tempered monoliths were cooled down to room temperature (approximate cooling rate: 2 K min^{-1}) to avoid tension within

Table 1
Composition of the suspension, used for the impregnation.

Component	Weight %
Polyvinyl alcohol (PVA)	1.17
Isopropyl alcohol	36.60
Hydrochloric acid (0.04 N)	35.14
Sodium chloride	1.46
Glass powder	25.63