Impact of pore structure on the thermal conductivity of glass foams

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Abstract

The thermal conductivity (λ) of glass foams is thought to depend on pore size. We report on the impact of pore size, determined using X-ray microtomography, and percentage porosity on the λ of glass foams. Glass foams were prepared by heating powder mixtures of obsolete cathode ray tube (CRT) panel glass, Mn_3O_4 and carbon as foaming agents, and K_3PO_4 as additive, to a suitable temperature above T_g, and subsequent cooling. Here, we report for the first time a correlation between λ and pore size in the range 0.10–0.16 mm showing a decrease from 57–49 mW m^{-1} K^{-1} with increasing the pore for glass foams with porosities of 87–90 %. This indicates that the pore structure should be optimized in order to improve the insulating performance of glass foams.

Keywords: Amorphous materials; Porous materials; Thermal properties; X-ray techniques

1. Introduction

Highly porous glass foams are an attractive insulating material owing to their thermal and sound insulating ability, and special properties such as freeze-thaw-cycle and fire resistance [1]. In addition, glass foams can be produced from waste glasses, e.g. obsolete cathode ray tube (CRT) glasses [2–4], which lack viable recycling possibilities. Glass foams from CRT panel glass exhibit low thermal conductivity (λ) [4,5]. However, the parameters required to optimise the conductivity of glass foams are poorly understood, outside of the obvious relationship of λ usually decreasing linearly with increasing porosity [5–7], whilst increasing with crystallinity [8].

In this study, we investigated the effect of pore size and porosity on thermal conductivity. Glass foams were prepared from a CRT panel glass-Mn_3O_4-carbon system with K_3PO_4 as additive. The additive plays a positive role in promoting the stability of closed pores for low-density glass foams [9]. To observe the effect of the pore size, we analyzed the 3D pore structure using X-ray microtomography (XMT).

2. Experimental

Powder mixtures were prepared using CRT panel glass powder, Mn_3O_4, carbon, and K_3PO_4 as described in Ref. [9]. Powder mixture (20 g) was uniaxially compressed at 40 MPa to obtain green bodies with 35 mm diameter. The green bodies were heated in N_2-atmosphere to 830 °C at 5 °C min^{-1}, dwelled for 15 min, and cooled below 500 °C at 10 °C min^{-1}. The glass foams were core drilled (diameter=44 mm), cut, and polished to obtain plane, smooth surfaces to measure the λ.

The porosity (ϕ_{exp}) and closed porosity (ϕ_{CP}) were calculated from the foam density (calculated from the mass and dimensions) and the skeletal and powder density (measured by He-pycnometry (Ultrapyc 1200e, Quantachrome)) as described in Refs. [5,9]. The λ was measured on glass foams using a transient plane souruce technique (TPS 2500s, Hot Disk) with a 5501 sensor (diameter of 6.403 mm) and a power and measurement time of 12 mW and 40 s, respectively. The sensor was placed between two samples. Each sample was measured five times with 15 min intervals to ensure temperature equilibration in the sample and then reporting an average value and standard deviation. The temperature was controlled at 25.4±0.1 °C by a climate chamber (WKL 100, Weiss).

The pore structure was analyzed using X-ray microtomography (XT H 225 ST, Nikon) operating at an accelerating voltage of 82–89 kV and a current of 84–93 µA, respectively. The spatial resolution was 7.62 µm/voxel (volumetric pixel). The 3D image visualization and pore size distribution were conducted using Avizo 9.0.0 software. The images were processed using a 3D median filter (averaging 26 nearby neighbors) three times to remove noise. The pore volume was measured in voxels, and calculated into equivalent sphere diameter (D_{eq}) [10] describing the diameter of a sphere with the same volume as the non-spherical pore analyzed. The struts and pore walls were analyzed on gold coated glass foam pieces using scanning electron microscopy (SEM; 1540 XB, Zeiss) operating at 10 kV.

3. Results

The pore structure of the glass foam without K_3PO_4 is shown in Fig. 1. Looking at the structure, pores in a broad size range are observed. A zoom on the sample (Fig. 1b) shows that the struts and pore walls are dense. This is in contrast to the SEM images, as seen in Fig. 1c, which reveal small pores in the struts and pore walls. The dense struts in the reconstructed images are due to the large voxel size (necessary in order to scan the large sample size) and image processing (i.e. median filtering). Despite the trade-off between sample size and resolution, X-ray microtomography remains to be preferred method for the analysis of the pore size distribution in glass foams due to its 3D view compared to the 2D view of SEM.

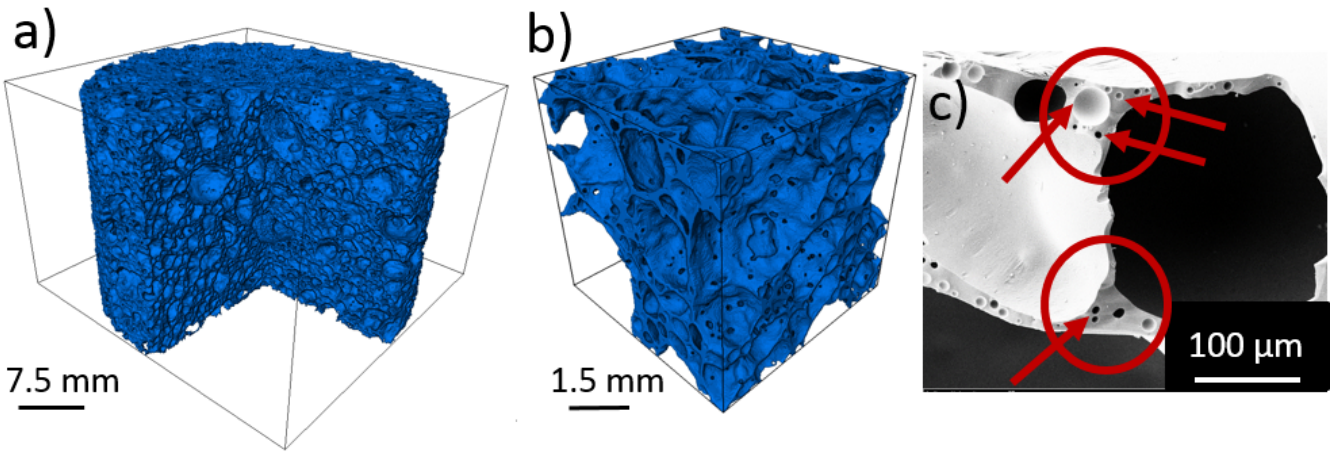

Fig. 1. 3D micrographic reconstructions of the pore structure of glass foam prepared without K_3PO_4 in a) full-size, b) subvolume, and c) SEM secondary electron image of struts (marked by circles), pore walls, and small pores inside struts (marked by arrows).

The size distributions show no correlation with the amount of K_3PO_4 in the tested range (Fig. 2). All samples have a broad size distribution (Fig. 2a) where four samples (K_3PO_4 content = 0, 0.34, 0.51, and 0.86 mol%) and three samples (K_3PO_4 content = 0.17, 0.68, and 1.03 mol%, dashed lines in Fig. 2a) show monomodal and bimodal distributions, respectively. The majority of the pores are <0.2 mm in diameter (Fig. 2a) while the main volume consist of pores ranging from 0.3–1 mm (Fig. 2b).

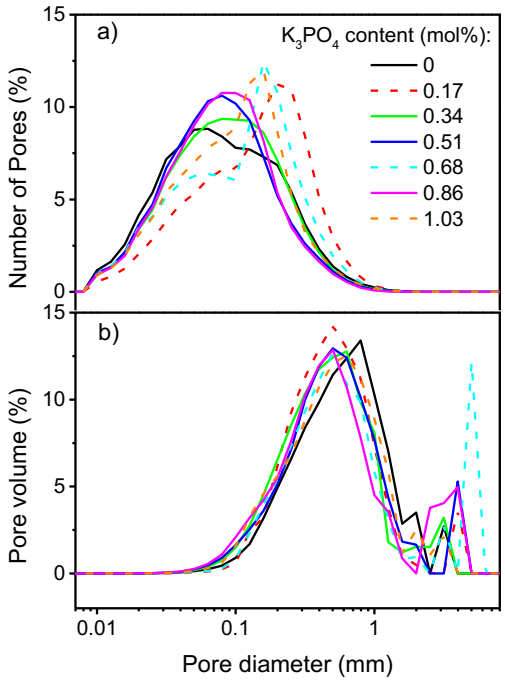

Fig. 2. Distribution of pore size (equivalent sphere diameter) of glass foams with different K_3PO_4 content (XMT data). a) Number of pores with bimodal distributions shown as dashed lines and b) pore volume. The pore diameter is in log space.

The experimental porosity of all samples is similar (87–90 %) and higher than the corresponding XMT porosity (70–78 %) due to the dense struts (Table 1). The closed porosity is high (>94 %) for all samples. The similar porosity is due to the similar chemical composition. The structural data show a difference in average diameter ranging from 0.10–0.16 mm while the maximum pore size is in the range of 3.26–5.99 mm indicating a moderate heterogeneity in the pore size distribution.

Table 1. Porosity from experiments (ϕ_{exp}) and XMT image analysis (ϕ_{XMT}), closed porosity ±1 point (ϕ_{CP}), and pore sizes based on D_{eq} ±0.1 mm of glass foams prepared with different content of K_3PO_4.

K_3PO_4 (mol%)	ϕ_{exp} (%)	ϕ_{XMT} (%)	ϕ_{CP} (%)	Avg. pore diameter (mm)	Max. pore diameter (mm)
0	89.6	71.3	97.3	0.11	3.42
0.17	88.1	73.5	94.9	0.16	3.98
0.34	87.9	71.6	95.4	0.11	3.48
0.51	87.2	70.3	95.2	0.10	4.50
0.68	88.9	77.3	96.3	0.13	5.99
0.86	87.6	71.0	95.1	0.10	4.14
1.03	88.0	75.0	96.2	0.12	3.26

In general, the λ decreases with increasing porosity of the samples (Fig. 3) in agreement with literature [5–7]. Though, the change is relatively small caused by the small change in porosity. However, a large deviation from the trend is found for two samples (triangles in Fig. 3).

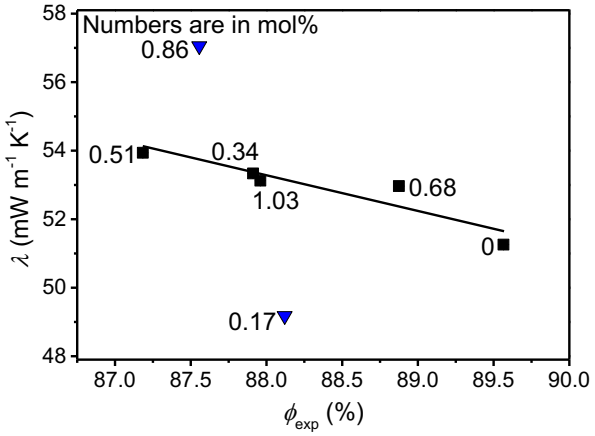

Fig. 3. Change in thermal conductivity (λ) with the porosity (ϕ_{exp}). The labels refer to the K_3PO_4 content. Outliers are marked with triangles. The errors are smaller than the symbols. The line is a visual guideline.

The porosity does not change with changing pore size of the glass foams (Fig. 4). In contrast, the λ continuously decreases from 57–49 mW m^{-1} K^{-1} with increasing average pore size from 0.10–0.16 mm. For the first time, a correlation between thermal conductivity and pore size is reported for this range of pores. The relatively large standard deviation of the pore sizes results in some uncertainty on the trend, however, the change in thermal conductivity is significant. In order to elucidate this

trend, futher studies need to be done with respect to the glass foams with a narrower size distribution of pores and an expanded range of pore sizes. Glass foams with increasing pore size from 1 to 5 mm show an increase in λ [11], which is expected considering the convection contribution of larger pores to heat transfer. Therefore, an optimum pore size must exist.

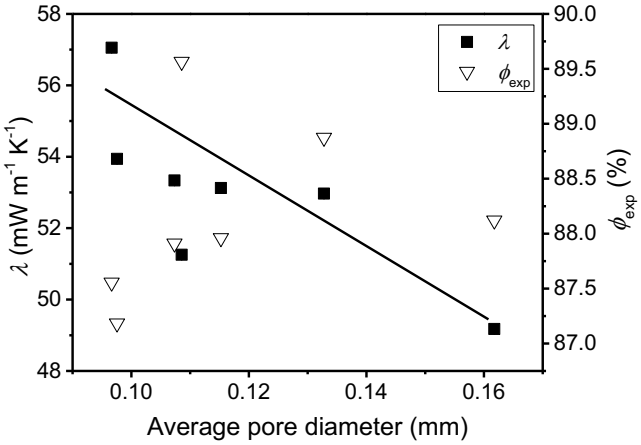

Fig. 4. Change in thermal conductivity (λ) and porosity (ϕ_{exp}) with increasing average pore diameter based on D_{eq}. Errors of λ and ϕ_{exp} are 0.1 mW m^{-1} K^{-1} and 0.1 point, respectively. The error of pore diameter is ±0.1 mm. The line is intended as visual guideline.

4. Conclusion

We prepared glass foams from a CRT panel-Mn_3O_4-C system with K_3PO_4 as additive. The pore structure is analyzed by X-ray microtomography in order to reveal its relation to porosity and thermal conductivity (λ). Preparing glass foams with varying pore size but similar porosity is difficult as the composition should be the same. The chemical composition was varied slightly to control the pore size while maintaining a near constant percentage porosity. The changing chemistry does not affect the properties, however, the average pore size varies by 60 %, ranging from 0.10 to 0.16 mm. A decrease of over 15 % in thermal conductivity (from 57 to 49 mW m^{-1} K^{-1}) occurs with a 60 % increase in pore size. Hence, a tailored pore structure can help to decrease the λ of glass foams.

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