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Influence of the glass particle size on the foaming process and physical characteristics of foam glasses

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ABSTRACT

We have prepared low-density foam glasses from cathode-ray-tube panel glass using carbon and MnO_2 as the foaming agents. The effect of the glass particle size on the foaming process, the apparent density and the pore morphology is revealed. The results show that the foaming is mainly caused by the reduction of manganese. Foam glasses with a density of <150 kg m^{-3} are obtained when the particle size is ≤33 μm (D50). The foams have a homogeneous pore distribution and a major fraction of the pores are smaller than 0.5 mm. Only when using the smallest particles (13 μm) does the pore size increase to 1–3 mm due to a faster coalescence process. However, by quenching the sample from the foaming to the annealing temperature the pore size is reduced by a factor of 5–10. The foams with an apparent density of <200 kg m^{-3} are predominantly open-porous. The foams exhibit a thermal conductivity as low as 38.1 mW m^{-1} K^{-1} at a density of 116 kg m^{-3}. For the investigated foam glasses, there exists a great potential to further decrease their thermal conductivity by increasing the closed porosity and by changing the trapped gas to CO_2.

1. Introduction

Foam glass is a highly porous (>85 vol.% pores), lightweight material used for thermal and acoustic insulation [1,2]. Depending on the application, e.g., heat insulation or soundproofing, the foam glass has predominantly closed or open porosity, respectively. Foam glass exhibits several advantages over conventional insulating materials such as organic foams and mineral wool, e.g., water and steam resistance, freeze-thaw tolerance, excellent chemical and thermal stability, high surface area and permeability, and superior mechanical properties. Due to the chemical stability and the high degree of closed porosity, the lifespan of foam glass (>100 years [3]) is much longer than conventional thermal insulation materials.

Foam glass is produced from powdered glass admixed with a foaming agent that releases gases at elevated temperatures. In the softened glass, the expanding gas bubbles increase the volume of the sample, thus forming a porous lightweight product. In industrial foam-glass production the majority of the glass originates from waste glass [1]. Some production facilities only make use of waste glass, thus eliminating the energy-consuming melting step. Foam-glass production makes it possible to recycle a great diversity of glassware or other amorphous materials into a high-value-added product. The waste glasses most commonly employed are mixed-color bottle glass [4–7] and window glass [8–12], but other glasses, like lamp glass [13], glasses from cathode ray tubes (CRTs) [14], fly ashes from coal production [15] and vitrified solid wastes from municipal waste combustion [16] can also be used. The foaming agent, added as a minor part to the powdered glass, releases gases based on a decomposition reaction or a redox reaction with the glass. The solid residues of the foaming agent or its reaction with the glass have an impact on the glass network and foam morphology. Therefore, foaming agents must be selected according to the composition of the glass.

Different foaming agents and/or their reactions with the glass lead to a wide variety of gases being found in the pores. In general, CO_2 is the best gas to be trapped in the pores, since it is easily obtainable, has a low thermal conductivity and a low toxicity. Gases like H_2O, O_2 and N_2 are also acceptable, but they have a higher thermal conductivity than CO_2. More problematic is the presence of CO, H_2 or SO_3 due to their high toxicity, flammability and/or reactivity. CO_2 gas is readily available from the decomposition of carbonates [8,14,17] and carbon-based foaming agents, like pure carbon materials, carbohydrates and SiC [1,18–20]. The latter are used by the foam-glass industry [1]. When carbon is used as a foaming agent, the gas released at elevated temperatures is a CO/CO_2 mixture, where the ratio depends on the availability of oxygen. During cooling the mixture then transforms to CO_2, according to Boudouard's equilibrium. When applying carbohydrates or SiC as a foaming agent, the gas-releasing mechanism becomes more complex [18,21]. For this reason, pure carbon is preferred over carbohydrates and SiC. The foaming starts after the glass has sintered to a state with closed pores, where the volume of the entrapped gases is too small for a successful foaming. Therefore, a sufficient amount of free oxygen has

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to be available from the glass melt. In order to promote the gas-releasing reaction, i.e., the oxidation of carbon, an oxidizing agent can be added, which acts as an oxidation/reduction couple with the carbonaceous foaming agent [10,11,22]. The most suitable oxidizing agents are Fe_2O_3 [10,16], MnO_2 [10,11,18] and sulfates [16,18,19]. However, the solid residues of the foaming agent can act as a nucleation and crystallization agent. This means that the impact of the foaming agent on the glass stability has to be considered.

Despite the fact that foam-glass technology has been known since the 1930s, the number of academic publications has only started to increase in the past 15 years. The main motivation for the research seems to be environmental consciousness and the increasing price of landfilling waste. The research on foam glass mainly concentrates on its mechanical properties, only few papers report on the thermal conductivity [9,14,15,21,23–26]. However, a worldwide focus on energy efficiency has put insulating properties higher on the agenda. Therefore, attention has been drawn to modified conventional and contemporary materials with improved insulating properties [27–29]. In order to promote the use of foam glass in thermal insulation, its insulating properties need to be enhanced.

The thermal insulation properties of a foam glass can be improved by (i) decreasing the density, (ii) closing the porosity, (iii) entrapping a low conducting gas, and (iv) employing glasses with a low thermal conductivity. To prepare a low-density foam glass (<150 kg m^{-3}), optimum conditions have to be found, i.e., a foaming agent compatible with the composition of the glass, an optimum concentration and the right heat-treatment conditions. Finely milled powder and homogenous mixtures result in small pores [6,30]. If the pores are closed, then convective heat transfer is prevented. Moreover, the viscosity as well as the surface tension should be in a defined range at the foaming temperature to support low density and small, closed pores [1,19]. When the pores are small and closed, the overall thermal conductivity of the foam glass can be estimated by summing the contributions from the conduction through the solid and the gaseous phases [31,32]. Based on an assumption of linear contributions [31,32] the difference in the thermal conductivity between a foam glass filled with O_2 (24 mW m^{-1} K^{-1}) and a foam glass filled with CO_2 (15 mW m^{-1} K^{-1}) [33] would be 8.6 mW m^{-1} K^{-1} for a foam glass with 95% porosity.

The effect of the particle size on the foam density and homogeneity is, despite being well known, scarcely reported [1,6,25,30,34]. It is common to report the particle size of the glass and the foaming agent before they are mixed. However, since the mixing is frequently carried out using milling equipment, the particle size changes, obscuring any clear relation between the particle size and the foam density. It was shown that when foaming with carbon the density of the foam glass decreases rapidly with a glass particle size below 100 μm [1,30]. On the other hand, the relationship between the particle size and the foam density is not so straightforward when using carbonates as the foaming agent [25].

The aim of the present work is to study the influence of the particle size on the foaming process and to prepare foam glasses with a low thermal conductivity. We foamed waste CRT panel glass with carbon and MnO_2 as the foaming agents. CRT panel glass has a high glass stability [25,35,36]. To reveal the influence of the particle size on the foaming process, pre-milled powder sieved to different fractions was mixed with the foaming agents and the mixture was homogenized without changing the particle size. In addition, the effect of the heat-treatment conditions on the characteristics of the foam and its stability are revealed and discussed. We characterized the apparent density, the closed porosity, the compressive strength and the thermal conductivity of the foam glasses.

2. Experimental

CTR panel glass was crushed in a jaw crusher (Retch BB51, Haan, Germany) and subsequently ball milled in a planetary ball mill (Retsch PM100). The powders were then sieved to obtain five powder fractions with different particle sizes using laboratory sieves (38–250 μm). The chemical composition of the CRT panel glass is reported elsewhere [25]. Carbon (activated charcoal; Bie & Berntsen, Søborg, Denmark) and MnO_2 (98%, Bie & Berntsen) were ball milled to pulverize the agglomerates and larger particles. The foaming mixtures were prepared from panel glass, 0.93 wt.% carbon and 6.76 wt.% MnO_2, according to previously determined optimum concentrations [37]. The carbon/MnO_2 ratio was equal to one-half of the stoichiometric amount needed for the theoretical carbon oxidation reaction:

$$C + 2MnO_2 \rightarrow CO_2 + 2MnO \qquad \text{(Reaction 1)}$$

The powder mixtures were homogenized on a carousel in a glass bottle with four light plastic balls for 17 h at 30 rpm. The particle size distribution of the powder mixtures was measured with a LS 13320 laser granulometer (Beckman Coulter, Brea, US-CA). The D50 and D90 values of the powder mixtures as well as the foaming agents are given in Table 1. The particle size distribution is shown in Fig. S1. Compared to the previous study [37], the powder processing in the present study was different, and thus the influence of the glass particle size on the foaming process could be revealed.

The powder mixtures were uniaxially pressed into disk-shaped pellets with 40 MPa. Small pellets (1 g, Ø = 13 mm) were used to study the influence of the particle size and the foaming conditions on the density and homogeneity of the foams. Larger pellets (Ø = 35 mm) of selected powder mixtures were used to prepare large samples (23–45 g) in a stainless-steel cylinder (6 cm in diameter and 5 cm in height) to study the thermal conductivity and compressive strength. The pellets were placed in an electrical laboratory-chamber furnace and heated at different heating rates (5 or 10 °C/min) to 835 °C and heat-treated for different times (5 to 30 min). Subsequently, the samples were cooled at 4 °C/min to the glass-transition temperature (T_g) of 530 °C [35] and then slowly cooled at 1 °C/min to room temperature. The temperature in the furnace was calibrated using an external thermocouple.

Thermogravimetic (TG) analyses were performed using a Jupiter 449 simultaneous thermal analysis (STA) instrument coupled with a 403C Aëoloss mass spectrometer (MS) (Netzch, Selb, Germany). The measurements were performed with a heating rate of 10 °C/min in an air atmosphere. The powder mixture was compressed with 40 MPa and a small piece (30–40 mg) was placed into an alumina crucible. The CO_2 peak was integrated to calculate the amount of carbon burnt out at the defined temperature.

The apparent density (ρ_{app}) of the small and the large foam samples was determined using Archimedes' principle in a 10 wt.% polyethylenglycol (PEG 3000 Da, Bie & Berntsen) solution or was calculated from the samples' mass and dimensions, respectively. A PEG solution was used to prevent absorption of the liquid medium during the measurement. The pycnometer density (ρ_{pyc}) of the foam samples was determined with a helium pycnometer (Ultrapyc 1200e, Quantachrome Instruments, Boynton Beach, US-FL). The powder density (ρ_{powder}) of the crushed foamed-glass sample was measured with the pycnometer. The percentage of the closed porosity, out of the

Table 1
Particle size (D50 and D90) of the powder mixtures, carbon and MnO_2.

Sample	D50 [μm]	D90 [μm]
#1	13	32
#2	33	80
#3	53	92
#4	103	163
#5	196	283
carbon	31	54
MnO_2	5.4	29