

Influence of concentration and dispersity of SiC addition on the structure and some properties of glass porous materials

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Porous materials were obtained from waste bottle glass with SiC additive. The effect of dispersity and concentration of the SiC additive, as well as the dispersity of the glass powder on the formation of the structure and properties of the materials were studied. As a result of the experiments on the synthesis of porous material from waste bottle glass and additive of silicon carbide carried out, it was found that the thermal treatment at 900 °C leads to the formation of porous glass-crystalline material. The apparent density, porosity and the microstructure of the samples were determined.

Key words: Waste glass, Microstructure, Porous materials.

Introduction

About 1.8 bln tons of wastes are annually generated in Europe but only one third of them are recycled [1]. The development of technologies for utilization of the wastes from the households, chemical, mining and manufacturing industries leads to solving ecological problems and has certain economic effect [2-5]. Waste glass has been used to obtain glass fibers, porous glass, glass ceramics and glass ceramic composites [6-10].

The most widely used method for production of porous materials from waste glass is based on sintering of dispersed powders wherein some additives as pore formers are added [11]. The pore forming additives are basically two types: dissociating and redox ones [12]. The former include salts and carbonates (CaSO₄, MgCO₃, CaCO₃) which decompose under heating and release gases. The redox additives are C-containing materials like coke, anthracite, graphite, carbon black, SiC, etc. During the heat treatment, these additives also release gases due to the oxidative reactions taking place [13-15].

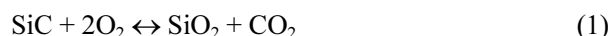
The present work aims to study the influence of the additive SiC on the formation of the structure of a porous material obtained from domestic waste bottles.

Experimental

The initial raw material used for the experiments was waste glass from bottles with chemical composition (mass%): 72,10 SiO₂; 2,00 Al₂O₃; 9,50 CaO; 2,00 MgO; 13,55 R₂O; 0,35 Fe₂O₃; 0,20 SO₃. The waste

glass was fritted by thermal shock and then milled in a ball mill (Retsch PM-4, Germany) at ratio glass : milling balls : water = 1 : 1,5 : 1 for 6 hours. After drying at 105°C, glass powders of dispersities < 63 μm and > 63 μm < 125 μm were used for the experiment.

The pore forming additive was technical SiC (β-SiC content-95%) with grain size 40 μm and 80 μm the pore forming effect of which results from an oxidative process described by the following equations [5]:



For the preparation of the porous product, several compositions were developed and their ingredients and dispersities are shown in Table 1. The samples were formed by pressing at pressure of 50 MPa. As temporary technological bonding, 8% solution of PVA was used. The thermal treatment of the samples was consistent with the transformation interval of the glass used (T_i - T_g), which was 800-950 °C (established by

Table 1. Composition of starting materials (mass%).

Composition	Dispersity of the glass, μm	SiC 40 μm	SiC 80 μm
1	> 63 μm	5	–
2	> 63 μm	10	–
3	> 63 μm	15	–
4	> 63 μm	20	–
5	> 63 < 125 μm	10	–
6	> 63 μm	–	10
7	> 63 < 125 μm	–	10

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DTA) and it was carried out in super kanthal oven Naber LHT, Germany at temperature of 900 °C. The heating rate was 10 °C/min and the isothermal period at the highest temperature was 30 min.

The phase composition of the products synthesized was determined by X-ray diffractometer (Philips PW1050) and the structural determinations were carried out with a scanning electron microscopes (Jeol JSM 6390).

The apparent density was measured by the hydrostatic method and the porosity was calculated by a standard technique [16]. The expansion process was examined by means of hot stage microscopy (HSM) on cylindrical specimens of 3 mm diameter and 4 mm height. Images of the specimens and data of the specimen height variation were taken at fixed intervals of temperature. The sintering curve displays the change in the specimen height related to the initial height, which is taken as 100%.

Results and Discussion

Visually, the products obtained had uniform porosity which, depending on the quantity and dispersity of the additive, consisted of pores of various sizes. Fig. 1 shows photographs of the macrostructures of samples containing 5, 10, 15 and 20 mass% SiC. It is seen that the pore size increased with SiC content which leads to disturbed uniformity of the structure (Fig. 1(d)).

For the composition with 5 mass% SiC, the amount of N_2 released was small according to Eqs.(1) and (2) and could not make the whole sample porous so some dense regions were observed (Fig. 1(a)). A homogeneous structure and high porosity were observed with 10 and 15 mass% SiC. Higher SiC concentrations lead to merging of pores and increase of their size which compromises the quality of the porous product.

The introduction of 15 mass% SiC was found to be the highest possible concentration for the formation of a homogeneous structure by these experiments. The apparent density and the total porosity of the samples are plotted in Fig. 2 and Fig. 3, respectively.

It can be deduced from the plots that the SiC additive had certain effect on the apparent density which decreases from 0.37 to 0.21 g/cm³ with the increase of

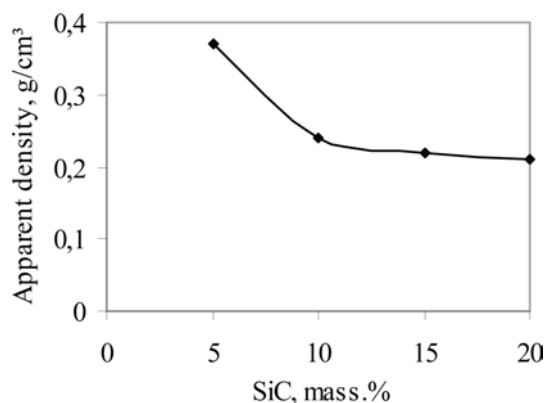


Fig. 2. Change of the apparent density depending on the amount of SiC.

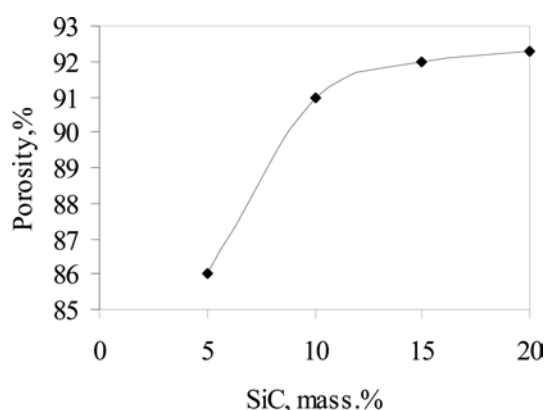


Fig. 3. Change of the porosity depending on the amount of SiC.

SiC content, while the total porosity increased to reach 92%. With the introduction of 5 mass% SiC, the value of ρ_{app} was 0.37 g/cm³ and the porosity was 86.1%. With the increase of the additive concentration to 10 mass%, the apparent density sharply decreased to about 0.24 g/cm³ with a porosity of 91%. Further increase of additive content (15 mass% and 20 mass%) gave minimal changes in the values of the apparent density and porosity. Namely, $\rho_{\text{app}} = 0.22$ g/cm³ and $P = 91.8\%$ at 15 mass% while for 20 mass% ρ_{app} was 0.21 g/cm³ and $P = 92.3\%$.

The volume changes of a sample containing 10 mass% SiC are shown in Fig. 4.

Sintering curve shows the change of sample height

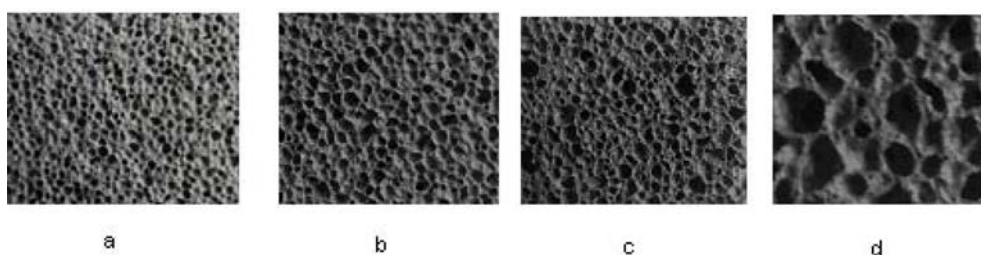


Fig. 1. Images of the macrostructure of samples containing; (a) 5 mass% SiC₄₀, (b) 10 mass% SiC₄₀, (c) 15 mass% SiC₄₀, (d) 20% mass% SiC₄₀.

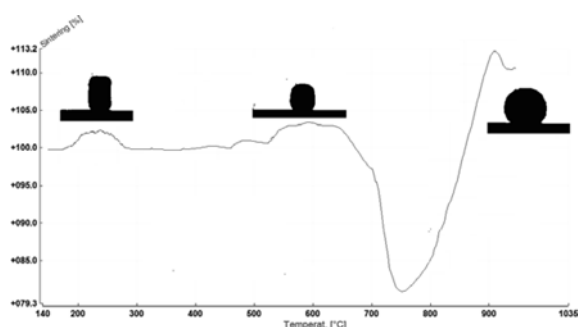


Fig. 4. Sintering curve by hot stage microscopy.

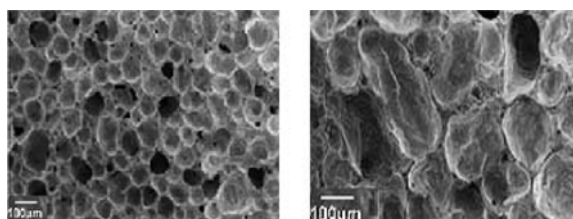


Fig. 5. Microstructure of samples containing 10 mass% SiC₄₀; (a) < 63 μm, (b) > 63 < 125 μm.

during the thermal treatment with respect to the initial height which was assumed to be 100%. The change (3%) in the temperature interval 180-300 °C resulted from the release of moisture present in the composition, as well as the decomposition of the technological bonding. The height remained constant until 600 °C. A change of 4% was observed in the interval 600-750 °C which was due to the initial oxidation of the SiC along Eqs. (1) and (2) [15].

Heating further to 700 °C, the sample was sintered and the height decreased. Above 800 °C the viscosity of the glass decreased which facilitated the reactions mentioned above.

The results obtained from HSM (Fig. 4 shows the volume changes of a sample in the temperature interval 140-950 °C) showed that 905 °C is the optimal temperature for the formation of porous structure. At this temperature, the glass powder makes a transition to plastic state and SiC is oxidized. The volume expansion of the sample was 15%.

The effect of glass dispersity on the microstructure of the materials synthesized is illustrated in Fig. 5.

At temperature of 900 °C and isothermal period of 30 min, it was found that the use of the same amount of SiC₄₀ with fine and a coarser fraction of glass powder, the latter gives material of higher apparent density (0.38 g/cm³). Using glass powder with dispersity < 63 μm and additive 10% SiC₄₀ (Fig. 5(a)), uniform porosity with spherical pores sized 50-150 μm was observed. Using glass powder of bigger particles (Fig. 5(b)), the pore size varied in the range 150-250 μm. The porosity here is less uniform, pores with elongated shape were observed.

The size of the pores decreased with the decrease of

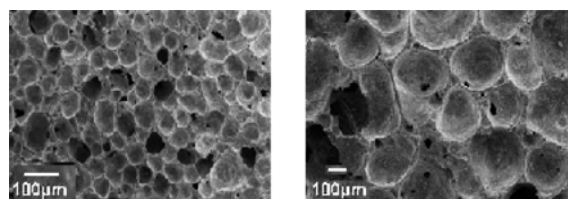


Fig. 6. Microstructure of samples; (a) SiC_{40im}, (b) SiC_{80im}.

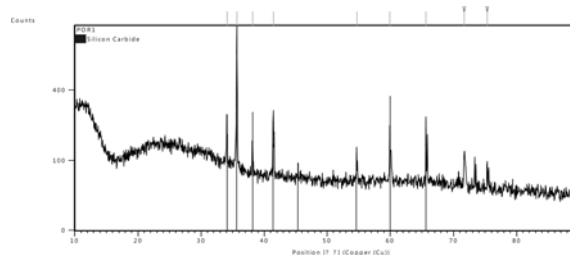


Fig. 7. Diffractogram of a sample containing SiC additive.

glass particles size. The small pore size and higher homogeneity obtained with finer glass particles was probably due to the fact that finer particles more readily pass into plastic state and oxidize SiC at higher rate. When the glass powder particles are larger than these of the additive (> 63 < 125 μm), the particles pass into plastic state at lower rate.

Fig. 6 shows SEM images of samples containing 40 im and 80 im SiC particles thermally treated at 900 °C. It can be seen from Figs. 6(a) and 6(b) that the smaller sized SiC particles gave higher number of pores. With the increase of additive particle size (SiC₈₀), the number of pores decreased while their size increased and the latter was in the range 400-700 μm (Fig. 6(a)). The smaller sized SiC particles were more easily homogenized in the glass powder and gave smaller amount of gaseous phase which lead to the formation of large number of smaller sized pores. According to König et al. [2], it is best to use equally sized glass powder and pore forming additive particles to achieve a homogeneous structure.

Consequently, the change of SiC particles size results in changes in the number, size and interconnectivity of the pores. Therefore, the decrease of the SiC particles size from 80 μm to 40 μm gives higher number of pores of smaller size, as illustrated in Figs. 6(a) and (b). This can be explained with the presence of larger number of SiC particles of smaller geometrical surface because of their smaller size.

Besides, it is harder to fully oxidize bigger SiC particles and this was established both visually by samples color and by X-ray phase analysis. The diffractogram in Fig. 7 shows a peak for non-oxidized SiC.

Conclusions

As a result of the experiments on the synthesis of porous material from waste bottle glass and additive of

silicon carbide carried out, it was found that the thermal treatment at 900 °C leads to the formation of porous glass-crystalline material.

The porosity formed depends on the dispersities of both glass powder and the additive. Certain effect exerts also the amount of additive introduced. The addition of SiC resulted in the formation of more uniform porosity and depending on the dispersity of the glass powder and the dispersity and amount of the additive, pores sized 50-700 µm were observed. The total porosity reached was 92%. The apparent density of the materials obtained varied from 0.21 to 0.37 g/cpm³ in combination with the synthesis temperature, providing the opportunities for these materials to be used for heat insulation applications in a working range up to 1000 °C.

With the present work, recycling of waste bottle glass into consumer product is achieved and certain ecological problem related to the utilization of domestic wastes is solved.

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