Research Article

Effects of Sb_2O_3 on the Mechanical Properties of the Borosilicate Foam Glasses Sintered at Low Temperature

Chenxi Zhai,¹ Zhe Li,² Yumei Zhu,¹ Jing Zhang,¹ Xiuduo Wang,³
Lejun Zhao,³ Liuming Pan,³ and Pengfei Wang⁴

¹Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

²School of Electronic Information Engineering, Tianjin University, Tianjin 300072, China

³Tianjin Municipal Engineering Design & Research Institute, Tianjin 300051, China

⁴State Key Laboratory of Transient Optics and Photonics, Institute of Advanced Materials, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Sciences, Xi'an 710119, China

Correspondence should be addressed to Yumei Zhu; tjuzhuyumei@gmail.com

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The physical properties and microstructure of a new kind of borosilicate foam glasses with different Sb_2O_3 doping content are comprehensively investigated. The experimental results show that appropriate addition of Sb_2O_3 has positive impact on the bulk porosity and compressive strength of the foam glass. It is more suitable in this work to introduce 0.9 wt.% Sb_2O_3 into the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ basic foam glass component and sinter at 775°C . And the obtained foam glasses present much more uniform microstructure, large pore size, and smooth cell walls, which bring them with better performance including a lower bulk density, low water absorption, and an appreciable compressive strength. The microstructure analysis indicates that, with the increase of the content of Sb_2O_3 additives, the cell size tends to increase at first and then decreases. Larger amounts of Sb_2O_3 do not change the crystalline phase of foam glass but increase its vitrification. It is meaningful to prepare the foam glass at a relatively low temperature for reducing the heat energy consumption.

1. Introduction

Foam glass has many excellent properties, such as light weight, suitable rigidity, high compressive strength, thermal insulation, chemical inertness, and nontoxicity [1–4]. However, the development of foam glass is slow. This is because its relatively low mechanical strength cannot satisfy the requirement of high strength in civil construction industry. Owing to this, the foam glasses are easy to break and fracture during the indispensable machining process [5].

Many efforts on improving the foam glasses' properties have been taken in recent years. The influences of glass compositions and different additives, including manganese dioxide, lead oxide, cobaltous oxide, chromic oxide, and antimonous oxide, on the density, microstructure, and mechanical properties of the foam glasses have been studied in

previous researches [6–12]. The impact of various experimental parameters on compressive property and porosity of glass-based foam composites has been investigated [13]. It is also reported that foams with a thermal conductivity as low as $0.060\text{--}0.070\text{ W/(m}\cdot\text{K)}$ have been prepared [14]. In addition, by adding just 1–2 wt.% carbonates and using low sintering temperature (850°C), foams with density and compressive strength values of about $0.36\text{--}0.41\text{ g/cm}^3$ and $2.40\text{--}2.80\text{ MPa}$ can be obtained [15]. Also, the influence of different experimental parameters on compressive strength and porosity of glass-based foam composites has been studied [16]. Taurino et al. investigated the effect of temperature on the sinter-crystallization ability of the borosilicate glass waste [17]. Lv et al. found that a faster heating rate tended to decrease the preoxidation of carbon black, resulting in an inhomogeneous foam distribution in the foam glasses [18].

Sb_2O_3 -containing foam glasses have excellent properties, for instance, low density and high strength. Sb_2O_3 -containing foam glasses with a density of 0.3 g/cm^3 can be obtained. The Sb_2O_3 -containing amount of the foam glasses is 0.6 wt.% [19]. Fan and Song have found that when the added amount of Sb_2O_3 is 0.2 wt.%–0.3 wt.%, the porosity of the foam glasses can be improved by 10–15% and the compressive strength can be improved by 20% [20]. It is also reported that Sb_2O_3 will release O_2 to accelerate the foaming when firing at high temperatures [21]. As a result, a higher porosity of the foam glasses will be obtained.

Du studied the effect of Sb_2O_3 on borosilicate foam glass when sintered at 1500°C . And it was found that the Sb_2O_3 -containing foam glass had attractive low density and high strength [19]. However, the traditional production method of foam glasses under high sintering temperature is of high energy consumption. For searching low temperature sintering methods, similar attempts had been tried on porous silicon carbide ceramics that had been fabricated at temperature as low as 800°C by a simple pressing and heat-treatment process [22].

A new method using chemically pure raw materials makes it easier to gain the relation between raw materials and products. In addition, finding a kind of raw materials that can reduce the energy wasted is important. Sb^{3+} has an electron structure of $18 + 2$ and this kind of structure has a strong ionic polarization. The strong ionic polarization can weaken the strength of Si–O bond and decrease the melt viscosity. This can help the pores grow. Through getting better structures, the properties of foam glass may be improved. Thus, Sb_2O_3 may be a good additive to foam glasses. Nevertheless, foam glasses sintered at low temperature with Sb_2O_3 as additive have not been reported.

In this work, we selected a new kind of low-temperature Na_2O – K_2O – B_2O_3 – Al_2O_3 – SiO_2 glass system to prepare the basic foam glass and investigated the effect of Sb_2O_3 additive on the mechanical property of the foam glass sintered at temperature lower than 850°C . We presented the results of a low-temperature foaming method of a powder mixture added carbon black as foaming agent, Na_2HPO_4 as foaming stabilizer, and Sb_2O_3 .

2. Experimental Procedures

2.1. Materials Preparation. The basic glass system had a weight percentage composition of 60SiO_2 – $13\text{H}_3\text{BO}_3$ – $5\text{Al}_2\text{O}_3$ – $17\text{Na}_2\text{CO}_3$ – $5\text{K}_2\text{CO}_3$. Additional 1 wt.% carbon black and 6 wt.% Na_2HPO_4 were added to produce the basic foam glass. At this base, different amounts of Sb_2O_3 (0 wt.%, 0.3 wt.%, 0.6 wt.%, 0.9 wt.%, and 1.2 wt.%, resp.) were added to the basic foam glass to obtain the foam glass compositions, marked as A, B, C, D, and E, respectively. All these raw materials are of analytical purity (Sinopharm Chemical Reagent Co., Ltd.) and have a mean particle size of about $100 \mu\text{m}$. The raw materials were mechanically mixed for 3 h by means of wet milling, with water as medium and a turning speed of 600 rpm. The obtained slurries were dried at 120°C for 4 h and then sieved with a 30-mesh sieve (particle size $\sim 550 \mu\text{m}$)

firstly. With further dry milling, finally the fine powders were obtained by sieving through a 150-mesh sieve (particle size $\sim 106 \mu\text{m}$). For preparation of the foam glass samples, the fine powders were placed in graphite crucible directly, heated up with the heating rate of $5^\circ\text{C}/\text{min}$, to a sintering temperature in the range of 750 – 800°C , and kept at the foaming temperature for 30 min. The obtained foam glass samples were naturally cooled down to room temperature and cut into samples for measurements.

2.2. Characterizations. The total porosity (P), foaming factor (α), and water absorption (WA) were calculated according to the following equation:

$$\begin{aligned} \%P &= \left(1 - \frac{d_b}{d_r}\right) \times 100, \\ \alpha &= \frac{(d_g - d_b)}{d_g}, \\ \text{WA} &= \frac{(g_s - g_l)}{(V \times \rho_w)}, \end{aligned} \quad (1)$$

where d_b and d_r are the bulk and the true density of the foam glass sample containing foaming agent and d_g is the bulk density of the sintered foaming agent-free sample. d_r was measured using the pycnometry method. g_s is the weight of sample before soaking and g_l is the weight measured after soaking in water. V is the volume of measured cubic sample and ρ_w is the density of water. To measure the WA value, the cubic samples were immersed into water for 2 h at room temperature.

The compressive strength was measured on a universal testing machine (XWW, Beijing Jinshengxin Detecting Instrument Co., Ltd., China) with a speed of $10 \text{ mm}/\text{min}$ on cubic samples with an average size of $11 \text{ mm} \times 11 \text{ mm} \times 11 \text{ mm}$. At least 5 tests were done for each sample to obtain the average value of density, WA, and the compressive strength. The fracture surface microstructure of the foam glasses was characterized by a scanning electron microscope (X-650, Japan). The crystallization degree of those foam glasses was analyzed by the X-ray power diffraction instrument (RigakuD/milx-3C) with Cu radiation in the 2θ range of 10 – 90° .

3. Results and Discussion

Table 1 gives the main physical properties of the foam glass samples produced at 775°C for 30 min, including the porosity (P), sintered bulk density (d_b), degree of foaming (α), compressive strength (σ), and water absorption (WA). It can be found that the density of foam glasses decreases at first and then increases, reaching the minimum value as the content of Sb_2O_3 is 0.9 wt.%. The values of WA for the different foam glass samples are small and show little change, which indicates that the pores mainly have a closed-cell structure and the addition of Sb_2O_3 has little influence on WA. However, the addition of Sb_2O_3 has a dramatic effect on the degree of foaming in these samples. From sample A to

TABLE 1: Main physical properties of the foam glass samples sintered at 775°C for 30 min.

Sample label	Sb ₂ O ₃ (wt.%)	<i>P</i> (%)	<i>d_b</i> (g/cm ³)	α	σ (MPa)	WA (%)
A	0	75.86 ± 1.000	0.507 ± 0.015	0.49 ± 0.010	3.64 ± 0.090	1.91 ± 0.040
B	0.3	82.08 ± 1.200	0.475 ± 0.010	0.61 ± 0.015	4.242 ± 0.090	1.73 ± 0.040
C	0.6	82.57 ± 1.200	0.462 ± 0.010	0.74 ± 0.015	4.274 ± 0.080	1.69 ± 0.030
D	0.9	84.6 ± 1.300	0.408 ± 0.010	0.81 ± 0.020	4.392 ± 0.090	1.57 ± 0.030
E	1.2	82.8 ± 1.100	0.469 ± 0.015	0.53 ± 0.010	4.642 ± 0.080	1.62 ± 0.030

P = porosity; *d_b* = sintered bulk density; α = degree of foaming; σ = compressive strength; WA = water absorption.

sample E, the degree of foaming increases by 60% and the porosity increases to 84.6%; at the same time, the bulk density and water absorption of the glass achieve their own minimum value. And mostly important, the compressive strength is also enhanced by about 20%. These results suggest that the foam glass with appreciable physical properties can be prepared at a relatively low temperature (less than 800°C).

With regard to the effect of Sb₂O₃ on lowering the sintering temperature, firstly, the Sb³⁺ cation has large polarization degree due to its 18 + 2 electrons outer electron shell structure. As Sb₂O₃ is added into the glasses, its strong polarization effect will weaken the Si–O bond. Thus, the viscosity of the glass decreases and the surface tension of the melted glass reduces [23], which lead to a decrease of the sintering temperature of the foam glass. On the other hand, the lowered viscosity and surface tension could accelerate the growing-up of pores from the melted glass, and thus pores are easier to grow up and become mutually combined. With more Sb₂O₃ added, even if there is no new phases present (see the XRD result below), the viscosity of the melted glass tends to decrease further. And this phenomenon will be more significant at 800°C. However, a much lower viscosity, that is, too much smaller surface tension, is unfavorable to form homogeneously distributed large size pores, and thus more amounts of small size pores were produced during the sintering process, resulting in the increase of density but decrease of porosity.

DSC/TG and XRD analysis on Sb₂O₃ powders (not reported here for the sake of brevity) showed that the Sb₂O₃ reacted with oxygen at about 500°C. In this case, the oxygen would react with Sb₂O₃ instead of carbon powder. Therefore, as a larger amount of Sb₂O₃ is added, it will also tend to inhibit the preoxidation of the carbon black during the heating-up process. Similarly, the deficiency of preoxidation of the carbon powders would bring about an inhomogeneous foam distribution in the foam glasses [18]. Figure 1 shows the fracture surface morphology of the foam glasses. Evidently, the amount of Sb₂O₃ in the batch dramatically influences the size, shape, and cell wall thickness of the pores in the glasses. With the increase of Sb₂O₃, the cell size shows a tendency of increase at first, followed by a decrease. Samples A and B have rather inhomogeneous microstructures with irregular pores and a few connected pores. Samples C and D present both an increase in the porosity and the cell size, and the cells maintain near-spherical shape and are mostly noninterconnected. The increase of cell size leads to a decrease in the thickness of the cell walls.

When the content of Sb₂O₃ is 1.2 wt.%, the microstructure returns to be inhomogeneous again. The small pores account for a large proportion reduced by the reduction of oxygen reacting with Sb₂O₃. From Figure 1, we can observe that the foam glass sample with composition D sintered at 775°C has the most homogeneous foam distribution. A detailed SEM image may further reveal the difference in morphology of the cell walls between samples A and D, as indicated in Figures 1(f) and 1(g). There exist large amounts of microcracks on the cell wall for sample A (without Sb₂O₃). In contrast, the cell wall for sample D (added with 0.9% Sb₂O₃) comes out to be smoother.

Figure 2 compares the effect of Sb₂O₃ content on the compressive strength of foam glasses heat treated at different temperatures. It is obvious that the compressive strength increases remarkably with the increasing addition of Sb₂O₃, and the lower heat treated temperature results in a much higher compressive strength for the samples with the same composition. As the foam glasses are sintered at 800°C, their compressive strength ranges from 1.8 MPa to 2.0 MPa, and the effect of adding Sb₂O₃ is tiny. When the sintering temperature decreases to 775°C, the compressive strength of each sample becomes almost twice. In this case, the minimum compressive strength increases to be 3.64 MPa, corresponding to the one without Sb₂O₃, and the maximum is 3.64 MPa for the one with 1.2 wt.% Sb₂O₃, which is increased by about 21.6%. This is probably due to the absence of visible deficiency such as microcracks observed on the cell walls [24], as indicated from Figure 1(g). However, the stress concentration at the microcrack tip will generally make the cell wall suffer cracking and tearing in the presence of external forces, leading to deterioration of the mechanical properties. As the microcrack becomes fewer, the stress concentration is easier to be avoided, and the compressive strength will increase. Further reducing the sintering temperature to 750°C, the compressive strength still increases but the enlargement is not so obvious.

Lowering the sintering temperature of foam glasses is important not only for improving the thermal efficiency, but also for avoiding the crystallization of the foam glass. That is because intense crystallization will hamper the foaming of the foam glass. To investigate the effect of Sb₂O₃ on the crystallization of foam glass, XRD measurement was performed for foam glass samples A and E sintered at different temperatures. As shown in Figure 3, the XRD patterns are quite similar, and each one consists of the characteristic peak of sodium aluminium phosphate (SAIP) and cristobalite

FIGURE 1: Fracture surface SEM micrographs of the foam glasses samples sintered at 775°C: (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) f is an observation of the cell walls at higher magnification in sample A, and (g) g is an observation of the cell walls at higher magnification in sample D.

FIGURE 2: Changes of the compressive strength with Sb₂O₃ content for the foam glass at different sintered temperatures.

FIGURE 3: XRD patterns of foam glass samples A and E sintered at 750°C, 775°C, and 800°C.

(SiO₂) and a board background corresponding to the silica-rich glass phases. It is suggested that the addition of Sb₂O₃ did not change the crystallization character of the basic foam glass system, which on the contrary benefited the vitrification of the foam glasses, due to its strong polarization and low melting point (~656°C). The XRD spectra also indicate that increasing sintering temperature causes a decrease of the intensity for the peaks of sodium aluminium phosphate and cristobalite.

4. Conclusions

The effects of Sb₂O₃ on the physical and mechanical properties were comprehensively investigated in this work.

The experimental results demonstrated that the bulk density of the investigated foam glasses decreased at first and then increased. The values of WA for the different compositions kept relatively stable. The addition of Sb₂O₃ also increased the compressive strength of the basic foam glass. It was more appropriate to introduce 0.9 wt.% Sb₂O₃ into the basic foam glass components and sinter the samples at 775°C. The obtained foam glasses presented more uniform microstructures and smooth cell walls, which bring the foam glasses better performance, such as a lower bulk density and a suitable compressive strength. The XRD results showed that the addition of Sb₂O₃ did not change the crystalline phase of foam glasses.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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