BOROSILICATE GLASS FOAM EXPERIMENTALLY MANUFACTURED BY MICROWAVE IRRADIATION

Marius Florin Dragoescu[1] and Lucian Paunescu[2]
[1] Daily Sourcing & Research SRL Bucharest, Romania, mar_dmf@yahoo.com
[2] Daily Sourcing & Research SRL Bucharest, Romania, lucianpaunescu16@gmail.com

ABSTRACT: A glass foam obtained by sintering at 790 ºC using borosilicate glass waste, carbon black (1%) as a foaming agent, Na_2HPO_4 (5.9%) as a stabilizing agent, Sb_2O_3 (0.8%) as an oxygen supplying agent and water addition (10%) as a binder was manufactured by microwave irradiation. The glass foam characteristics were: apparent density of 0.34 g/cm^3, porosity of 84.5%, thermal conductivity of 0.06 W/m·K, compressive strength of 2.2 MPa. The pore size was between 0.4-0.7 mm. The specific consumption of energy had an extremely low value (0.68 kWh/kg) below the level of the consumptions of glass foam industrially made by conventional techniques.
KEYWORDS: glass foam, microwave, borosilicate glass waste, disodium phosphate, antimony oxide, specific consumption of energy.

1. INTRODUCTION

Due to its characteristics (low thermal expansion, high chemical resistance in corrosive environments, acid resistance, durability) the borosilicate glass is commonly used in chemical laboratory equipment, cookware, lighting and in certain kinds of windows [1]. About three million tons of borosilicate glass were produced in the EU countries in 2009, representing 10% from the total production of glass. The borosilicate glass waste constitutes the raw material for manufacturing the borosilicate glass foam applicable in industry to produce anti-corrosive equipment, lining and thermal insulating due to many advantages: low coefficient of thermal expansion, small density, low thermal conductivity, good thermal stability, chemical stability, excellent electrical performances [2]. Several works in the literature present technical solutions for the manufacture of glass foam from borosilicate glass waste. Carbon black is commonly used as a foaming agent [3]. Also, oxygen releasing agents as SO_3 (in the glass composition) and iron oxide (Fe_2O_3) or antimony oxide (Sb_2O_3) as additives are needed to improve the foaming. The grain size of the carbon black must be below 150 μm and the heating rate of the powder mixture is recommended at 8 ºC/min to obtain a homogeneous porous structure of glass foam [4].

Experimental results obtained in the manufacture of glass foam using borosilicate glass waste as raw material, carbon black as foaming agent, disodium phosphate (Na_2HPO_4) as stabilizing agent and Sb_2O_3 as oxygen supplying agent in varying proportions are presented in [5]. Optimal results were obtained at 775 ºC with an addition of 0.9% Sb_2O_3. The density of the foamed material was lower, also the water absorption was reduced and the microstructure of the sample was more uniform. A high compressive strength (4.4 MPa) was obtained. The main crystalline phase of the sintered foam at 775 ºC was sodium aluminum phosphate and to a lesser extent cristobalite. It has been found that higher proportions of Sb_2O_3 do not change the crystalline phase, but increase the vitrification of the foam.

Glass foam prepared by sintering (at 1200 ºC for 30 min) a powder mixture containing borosilicate glass waste, carbon black (0.9%) and Sb_2O_3 (8.1%) as foaming agents was performed [2]. The foamed samples had a homogeneous pore distribution with dimensions between 0.2-1 mm. The bulk density was 0.5 g/cm^3 and the water absorption was very low (0.4%). The average thermal expansion coefficient had the value $9.22 \cdot 10^{-6}$/ºC. The acidproof test showed a good acid corrosion resistance.

The effect of Sb_2O_3 on the properties of borosilicate glass foam obtained by sintering the waste at 1500 ºC was studied [6]. Low density (0.3 g/cm^3) and high mechanical strength were obtained for a Sb_2O_3 content of 0.6%.

It was found that for 0.2-0.3% addition of Sb_2O_3 the porosity of the glass foam can be increased by 10-15% and the compressive strength by 20% [7].

Manufacturing results of glass foam by sintering at low temperature of a borosilicate glass waste with an organic binder as a foaming agent [8] are presented in literature. The crystallization process was initiated at 845 ºC and was completed at 900 ºC. Wollastonite and cristobalite were identified as crystalline phases.

The foamed product had a porosity around 78-79%, an apparent density of about 0.5 g/cm^3 and a porous closed-cell microstructure, being used as a thermal insulating material.

All the experiments presented in the literature and mentioned above were performed by conventional heating techniques (with fossil fuel consumption or with electrical resistances).

The manufacture of a reinforced glass foam with metal fibres using borosilicate glass waste and nickel-based alloy fibres was experimentally investigated on an own conception microwave equipment operating at a frequency of 2.45 GHz [9]. The power of the microwave generator could be continuously varied within the limits of 300-3000 W. The glass/metal composite samples were thermally protected with a silico-aluminous refractory lining and an addition of alumina powder. A silicon carbide (SiC) disc was used as an auxiliary microwave absorber. The power dissipated in the system was measured at 600-650 W compared to the maximum value of a magnetron of 800 W. The test results showed that a maximum volumetric fraction of metal fibres of 10% led to an improvement in the distribution of smaller pores in the structure of the material. Samples made with 10% fibres using the SiC microwave absorber were the best. The fibres were thought to act as nucleating agents for pore formation. Sintering took place in less than 3 minutes. The combination of high porosity and toughening with metal fibres has led to composites with high resistance to thermal shock suitable for thermal protection systems. According to the authors of the paper, the results presented are in an intermediate stage and a series of other tests would be performed further.

A recent paper (2019) made by the authors of the current paper presents experimental results obtained in the manufacturing process of glass foams from borosilicate glass waste using microwave irradiation as energy source [10]. The experiments were performed on a 0.8 kW-microwave oven of the type used in the household adapted for high temperature operation. During the experiments, three types of foaming agent were successively used as well as various mineral additives to improve the foaming. Thus, one variant included 3% SiC as a foaming agent and 9.1% coal ash, another had 1.3% $CaCO_3$ as a foaming agent and the last variant used 1% activated carbon as a foaming agent and 6.2% Na_2HPO_4 as a fluidizing agent. The sintering-foaming processes occurred at 970, 830 and 820 ºC respectively. The most advantageous variant in terms of material quality and energy consumption was the last. The characteristics of the glass foam were: apparent density of 0.34 g/cm^3, thermal conductivity of 0.055 W/m·K and compressive strength of 2.5 MPa. The microstructure of the glass foam sample was homogeneous, the pore size being 1-2.5 mm. The specific energy consumption was 2.84 kWh/kg, the value being relatively high due to the small amount of raw material (250.6 g) compared to the available power of the oven (0.8 kW).

The research in the field of glass foam manufacturing, focused in the last three years on the application of an nonconventional technique (microwave energy) by the Romanian company Daily Sourcing & Research, has shown on an experimental scale (under specific unfavorable conditions) an energy efficiency at least similar to that of the industrial production of glass foams of the same type. The microwave heating process is practically unused in the glass industry.

The paper aimed to manufacture a glass foam with physical, mechanical and morphological characteristics superior to those previously obtained, in improved conditions of microwave irradiation, in order to reduce the specific energy consumption below 1 kWh/kg.

2. METHODS AND MATERIALS

2.1 Methods

Previous experiments of heat treatment of glass-based raw material highlighted the need to create the conditions for a mixed microwave heating (partly direct, partly indirect), on the one hand, in order not to cause serious damage to the internal structure of the glass due to excessive intensity of contact between the microwave field and the material and, on the other hand, to ensure a sufficiently high energy input aiming a maximum thermal effect with minimum energy consumption. This objective can be achieved by placing between the microwave emission source and the material of a ceramic tube from a SiC-based material with a wall thickness of 3.5-5 mm, which allows both the penetration of a certain proportion of electromagnetic waves and the absorption in the ceramic tube mass of the rest of the microwave field. In both cases, the electromagnetic waves are converted into heat. The heating of the material takes place both from inside it to its peripheral areas (the direct heating) and through the radiation of the hot inner surface of the tube to the material (the indirect heating).

To be functional, the constructive scheme of the experimental microwave equipment presented in Figure 1 must have a very efficient thermal

protection system of the hot zone containing the material subjected to heating. Heat-resistant ceramic fibre mattresses (at 1200 ºC) were used for this purpose, being placed at the base of the oven, around the ceramic tube and above the ceramic lid made of the same material as the tube. The process temperature control was performed with a radiation pyrometer mounted above the oven. The upper wall of the oven, the ceramic lid and the mattress that protects the lid had holes with a diameter of 30 mm to facilitate the visualization with the pyrometer of the surface of the heated material.

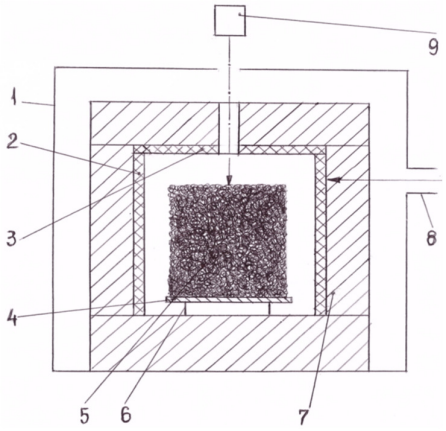


Figure 1. The experimental microwave equipment

1 – 0.8 kW-microwave oven; 2 – ceramic tube; 3 – ceramic lid; 4 – metal plate; 5 – pressed powder mixture; 6 – metal support; 7 – ceramic fibre mattress; 8 – magnetron waveguide; 9 – radiation pyrometer.

2.2 Materials

The materials used in these experiments were: borosilicate glass waste as raw material, carbon black as a foaming agent, disodium phosphate (Na_2HPO_4) as a stabilizing agent and antimony oxide (Sb_2O_3) as an oxygen supplying agent. A similar composition of materials was used in the experiments presented in [5], but performed by a conventional heating technique.

The chemical composition of the borosilicate glass waste including mainly laboratory glass waste was: 71.5% SiO_2; 12.7% B_2O_3; 2.6% Al_2O_3; 5.8% Na_2O; 0.2% K_2O; 4.1% CaO; 2.1% MgO; 0.2% Fe_2O_3; 0.8% TiO_2. The glass waste was crushed, ground in a ball mill and sieved at a grain size below 63 μm.

Carbon black is virtually pure elemental carbon in the form of colloidal particles [11]. The commercial carbon black used in experiments had a grain size below 18 μm.

The disodium phosphate was ground in a laboratory electrical device and sieved at a grain size below 63 μm.

The antimony oxide (Sb_2O_3) was ground in the laboratory device and sieved at a grain size below 63 μm.

2.3 Characterization of the glass foam samples

The glass foam samples experimentally obtained by the sintering-foaming process of borosilicate glass waste were characterized by traditional analysis methods. The main physical, mechanical and morphological characteristics were: apparent density, porosity, thermal conductivity, compressive strength, water absorption, crystallographic structure and microstructural configuration of the samples. The apparent density was measured by the gravimetric method [12]. The porosity was calculated by the comparison method between the porous sample density and the density of the same material type in compact state [13]. The thermal conductivity was determined by measuring the thermal flow that passes through a sample placed between two metal plates (one heated and the other cooled) [14]. The compressive strength was determined using an uniaxial press and the water absorption of the samples was measured by the traditional method of their water immersion (ASTM D 570). The X-ray diffraction (XRD) was used according to the standard EN 13925-2:2003 to determine the crystallographic structure of the samples. A X-ray diffractometer Bruker AXS D8 Advance with CuKα radiation was used. The porous microstructure was identified with a Smartphone Digital Microscope.

3. RESULTS AND DISCUSSION

3.1 Results

Four experimental variants were adopted according to Table 1. Carbon black was kept constant at 1 wt.%. Na_2HPO_4 varied between 5.8-6.1 wt.% and Sb_2O_3 had values in the range 0.6-1.2 wt.%. The borosilicate glass waste varied between 91.7-92.6 wt.%. Water addition as a binder was used in a constant ratio (10.0 wt.%) for all variants.

Table 1. The adopted experimental variants

Component	Variant 1	Variant 2	Variant 3	Variant 4
Borosilicate glass waste, wt.%	92.6	92.3	92.0	91.7
Carbon black, wt.%	1.0	1.0	1.0	1.0
Na_2HPO_4 wt.%	5.8	5.9	6.0	6.1
Sb_2O_3 wt.%	0.6	0.8	1.0	1.2
Water addition wt.%	10.0	10.0	10.0	10.0

The main functional parameters of the manufacturing process of glass foam presented in Table 2 include the raw material amount, the sintering-foaming temperature, the heating time, the heating and cooling rate, index of volume growth, the glass foam amount and the specific energy consumption.

Table 2. The functional parameters of the process

Parameter	Variant			
	1	2	3	4
Raw material amount (g)	550	550	550	550
Sintering-foaming temperature (ºC)	783	790	798	805
Heating time (min)	30	31	33	36
Heating rate (ºC/min)	25.4	24.8	23.6	21.8
Cooling rate (ºC/min)	6.3	6.5	6.2	6.2
Index of volume growth	1.75	1.90	2.10	2.25
Glass foam amount (g)	534	535	533	537
Specific energy consumption (kWh/kg)	0.66	0.68	0.72	0.78

According to the data in Table 2, the adoption of an optimal amount of powder mixture loaded in the oven (550 g for each variant) adequate to its available power (0.8 kW) led to obtaining quantities of foamed products between 533-537 g, significantly reducing the value of specific energy consumption (0.66-0.78 kWh/kg) at a level below that estimated in the literature [15] for the industrial production of glass foam (0.80-0.85 kWh/kg). Based on the considerations stated in another bibliographic source, the difference between the energy efficiency of an industrial microwave equipment compared to a low power microwave oven used in the household, similar to that adapted for the experiments described above, could reach almost 25% [16].

The temperature of the sintering-foaming process was relatively low (maximum 805 ºC) and the process time was between 30-36 min. Due to the very high thermal protection of the work space with high-performance ceramic fibre mattresses, avoiding to a large extent the heat loss outside the system, the heating rate of the material was in the range of 21.8-25.4 ºC/min. The increase in volume due to foaming was in the normal limits between 75-125%.

The physical, mechanical and morphological characteristics of the glass foam samples are shown in Table 3 including the apparent density, porosity, thermal conductivity, compressive strength, water absorption and pore size.

Table 3. Physical, mechanical and morphological characteristics of the glass foam samples

Characteristic	Variant			
	1	2	3	4
Apparent density (g/cm3)	0.36	0.34	0.35	0.33
Porosity (%)	83.6	84.5	84.0	85.0
Thermal conductivity (W/m·K)	0.063	0.060	0.059	0.060
Compressive strength (MPa)	2.6	2.2	2.1	1.8
Water absorption (%)	2.4	2.3	2.6	2.7
Pore size (mm)	0.3-0.6	0.4-0.7	0.7-1.0	0.8-1.2

According to Table 3, the glass foam samples had low values of the apparent density (0.33-0.36 g/cm^3) as well as of the thermal conductivity (0.059-0.063 W/m·K). Implicitly, the porosity of the four samples had high values (83.6-85.0%). Due to the boron content of the glass waste, the compressive strength was quite high (1.8-2.6 MPa), the higher the value corresponding to sample 1 with the higher apparent density. Referring to the water absorption, sample 4 showed the highest permeability (2.7%), but generally, all samples were at a similar level (2.3-2.7%) being considered with a high degree of impermeability.

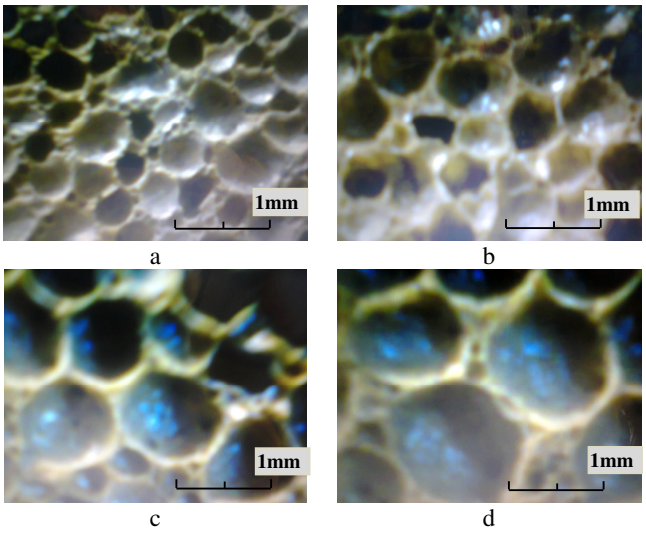
The cross section of the glass foam samples, shown in Figure 2, indicated homogeneous porous microstructures with small pore sizes. Sample 1, with the lowest ratio of oxygen supplying agent for carbon black (0.6% Sb_2O_3) had the finest porosity, the pore size being between 0.3-0.6 mm. Sample 4, with the highest ratio of Sb_2O_3 (1.2%) had a microstructure with larger pores (between 0.8-1.2 mm).

The microstructural configuration of the glass foam samples is shown in Figure 3.

a b c d

Figure 2. Cross section of the glass foam samples

a – sample 1, heated at 783 ºC; b – sample 2, heated at 790 ºC; c – sample 3, heated at 798 ºC; d – sample 4, heated at 805 ºC.



a b c d

Figure 3. Microstructural configuration of the samples

a – sample 1, heated at 783 ºC; b – sample 2, heated at 790 ºC; c – sample 3, heated at798 ºC; d – sample 4, heated at 805 ºC.

The main crystalline phases of the four glass foam samples sintered at 783-805 ºC identified by the XRD analysis were sodium aluminium phosphate and to a lesser extent cristobalite. The increase of the Sb_2O_3 ratio in the powder mixture of raw material from 0.6 to 1.2 wt.% did not change the composition of the crystalline phase.

Variant 2 made with 1% carbon black, 0.8% Sb_2O_3 and 5.9% Na_2HPO_4 was considered optimal having the apparent density 0.034 g/cm^3, porosity 84.5%, thermal conductivity 0.06 W/m·K and compressive strength 2.2 MPa. The pore microstructure was homogeneous, composed from closed pores with dimensions between 0.4-0.7 mm. The sample embeds the appropriate characteristics to be used as an insulating material in construction. The specific consumption of energy to manufacture this variant was extremely low (0.68 kWh/kg), below the level of glass foam consumptions industrially made by conventional methods.

3.2 Discussion

The microwave heating process known since the middle of the 20th century has been applied on a small scale and generally, at relatively low temperatures. Only in the last 10-15 years it has been experimentally found that several materials are suitable for microwave heating: ceramics, organics, polymers, metals, glasses, etc. [16]. However, industrial applications of microwave heating at high temperatures do not yet exist. All the results are on an experimental scale. The suitable materials for microwave heating are those that have appropriate dielectric properties (high electrical conductivity and dielectric loss factor). They efficiently absorb the electromagnetic radiation and convert it into heat. Some inorganic oxides and most carbonaceous materials are excellent microwave absorbers [17]. The main advantages of the microwave heating compared to the conventional heating are: higher heating rate, selective heating (i.e. heating only the material subjected to this process, not other massive components of the oven), better control on the heating, low dimensions of the equipment [18].

Comparing the characteristics of sample 2 considered optimal with a glass foam also produced in the microwave oven from borosilicate glass waste, activated carbon (1%) and Na_2HPO_4 (6.2%) sintered at 820 ºC [10] results that these are close, except for the larger pore size at the reference sample (between 1-2.5 mm) and the much higher specific energy consumption in the case of the reference variant (2.84 kWh/kg).

4. CONCLUSION

A glass foam obtained by sintering at 790 ºC using borosilicate glass waste, carbon black (1%) as a foaming agent, Na_2HPO_4 (5.9%) as a stabilizing agent, Sb_2O_3 (0.8%) as an oxygen supplying agent and water addition (10%) as a binder was manufactured by microwave irradiation.

The glass foam physical, mechanical and morphological characteristics were: apparent density-0.34 g/cm^3, porosity-84.5%, thermal conductivity-0.06 W/m·K, compressive strength-2.2 MPa and pore size between 0.4-0.7 mm.

The physical, mechanical and morphological characteristics of glass foam made of borosilicate glass waste are suitable for using as an insulating material in construction.

Due to the efficient use of the microwave irradiation the specific consumption of energy had an extremely low value (0.68 kWh/kg) below the level of the consumptions of the glass foam industrially made by conventional techniques.

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