HIGH MECHANICAL STRENGTH CELLULAR GLASS-CERAMIC MANUFACTURED IN MICROWAVE FIELD USING BLAST FURNACE SLAG AND GLASS WASTE

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ABSTRACT: A cellular glass-ceramic with very high compressive strength (14.1 MPa) from a mixture 40/60 of blast furnace slag and container glass waste, calcium carbonate (6.5%), borax (7.8%), titanium oxide (5%), sodium phosphate (3%) and water addition (8%) was experimentally manufacture by sintering at 900 ºC using the microwave radiation. The main advantage of the nonconventional heating technique was the very low specific energy consumption (0.90 kWh/kg). The physical, mechanical and morphological characteristics of the best cellular glass-ceramic sample were: apparent density of 0.82 g/cm^3, porosity of 75.9%, thermal conductivity of 0.135 W/m·K, water absorption of 3.4%, pore size between 0.3-0.6 mm. Due to the mentioned characteristics the cellular glass-ceramic is suitable for construction applications.
KEYWORDS: cellular glass-ceramic, microwave, blast furnace slag, glass waste, compressive strength, specific energy consumption.

1. INTRODUCTION

The glass-ceramics are fine-grained polycrystalline inorganic materials produced by a high-temperature heat treatment of glasses with a suitable composition for a controlled crystallization. Most silicate-based wastes (blast furnace slag, fly ash, mud from zinc hydrometallurgy, oil shale by-products, glass waste, etc.) have the potential for the production of glass-ceramics by the additional incorporation of some additives to correct the chemical composition of the parent glass. An important advantage of glass-ceramics compared to the parent glasses are their superior physical and mechanical properties. Usually, this is the direct result of their polycrystalline structure. The microstructure of a glass-ceramic is not completely crystalline, the rest being residual glass. One or more crystalline phases can be formed during the heat treatment having different compositions compared to those of the parent glass [1]. The cellular glass-ceramic is a porous, light weight material with high mechanical strength. It also retains the other remarkable characteristics of glass foam (resistance to fire, water, corrosion, attack of external agents, non-toxicity, etc.) [2]. Certain chemical compounds (TiO_2, ZrO_2 or CaF_2) are used as nucleating agents. The nucleating process takes place at lower temperatures and precedes the crystallization process at higher temperatures [1, 3].

According to the literature, the high temperature sintering (about 900 ºC) of blast furnace slag mixed with glass waste is a method experimentally used in the world to produce a cellular glass-ceramic with very high mechanical strength. A blast furnace slag with high content of TiO_2 (20-27%) granulated by water cooling was used as raw material together with glass waste in the ratio 30/70 [2]. Calcium carbonate ($CaCO_3$) was adopted as a foaming agent, borax ($Na_2B_4O_7 \cdot 5H_2O$) as a fluxing agent and sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) as a stabilizing agent. The materials were mixed in a ball mill and mechanical pressed in a small dimension mold. The heat treatment consisted in a heating at 400 ºC with the rate of 5 ºC/min, followed by the final heating with 10 ºC/min at 900 ºC kept for 30 min. An important role in the sintering process had borax used between 6-10%. The best results were obtained for 8% borax: bulk density 0.82 g/cm^3, compressive strength 25 MPa, structural homogeneity with pore size between 1.0-1.2 mm. The increase of the borax ratio leads to the increase of bulk density at 0.96 g/cm^3 and decrease of the compressive strength up to 9 MPa, the pore size increasing very much and having an uneven distribution.

A cellular glass-ceramic was manufactured by the powder sintering technology at 900 ºC using titanium-rich blast furnace slag and glass waste as the main raw materials. In addition, $CaCO_3$, borax and sodium phosphate were used. According to the research results, the increase of the $CaCO_3$ content made the foaming process harder, with a more uniform porous structure. As a result, compressive strength and bulk density increased, while porosity

and water absorption decreased. Homogeneous porous structures and optimal comprehensive properties were achieved with 5-7% $CaCO_3$, the bulk density having values in the range 0.79-0.82 g/cm^3, the porosity being between 73.1-75.3%, the water absorption between 3.3-3.8% and the compressive strength between 13.1-13.9 MPa [4].

Cellular glass-ceramics were produced using blast furnace slag and glass waste as raw materials. TiO_2, ZrO_2 and CaF_2 were chosen as nucleating agents. Calcium carbonate (about 6 wt.%) as a foaming agent, sodium phosphate as a stabilizing agent and borax as a fluxing agent were added to the raw material powder mixture. The experimental results showed that the glass-ceramic foam with 50 wt.% blast furnace slag showed excellent comprehensive properties (bulk density of 0.79 g/cm^3, water absorption of 2.71% and bending strength of 14.34 MPa) [3]. The role of TiO_2 and ZrO_2 used as nucleating agents in the glass-ceramic manufacturing process were revealed in the literature. According to Reben et al., TiO_2 is effective in decreasing the crystallization temperature, while ZrO_2 increases it [5].

The tailing microcrystalline foam glass is a building material, which has not only the characteristics of a light weight material, fire resistant and thermal insulating, but also decorative applications. The research has shown that the foaming agent (silicon carbide) has a great influence on the mechanical properties of the material. By reducing the proportion of SiC, the material strength increased. The surface of the microcrystalline decoration has improved the flexural strength and the compressive strength. The bulk density had low values (0.3-0.4 g/cm^3), the porosity was high (85.2-87.5%), the water absorption was between 1.8-2.4% and the thermal conductivity was in a very wide range (0.075-0.380 W/m·K). The compressive strength had very high values between 4.0-12.5 MPa [6].

All the experimental results presented above were obtained on a small scale. The industrial cellular glass manufacturers have not yet shown interest in using blast furnace slag as a raw material. The heat treatment of blast furnace slag and glass waste was achieved by conventional energy consumption. None of the bibliographic sources mentioned the value of the specific energy consumption, but in the conditions of a thermal efficiency lower than 20% its value cannot be below 1.38 kWh/kg, taking into account that the heating to 900 C of a mixture of blast furnace slag and commercial glass (soda-lime glass) in equal proportions requires a theoretical consumption of 0.276 kWh/kg [7].

In the last three years, a research team from the Romanian company Daily Sourcing and Research has focused its activity on the production of cellular glass by using the microwave energy. Known since the mid-20th century, the microwave radiation has been used to a very small extent and only in drying and low temperature heating processes, although their application has confirmed that it is a fast, "clean" and economical process. In the last 10-15 years, it has been found that several types of material (ceramics, organics, metals, polymers, glasses, etc.) are suitable for efficient microwave heating [8].

The current paper shows experimental results obtained by authors in the field of manufacturing by a nonconventional technique of glass-ceramics using blast furnace slag and glass waste as raw material. The research aimed to produce a cellular material with high mechanical strength for construction applications obtained from recycled industrial or commercial waste by using the microwave energy, more efficient than the conventional energy [8].

2. METHODS AND MATERIALS

2.1 Methods

The principle of obtaining a cellular glass from a powder mixture of silicate materials consists in incorporating in this mixture a finely ground foaming agent and heating to the sintering temperature of the mixture. The foaming agent (various forms of carbon, calcium carbonate, silicon carbide, etc.) releases a gas or a gaseous compound by a reaction of decomposition or oxidation in a suitable viscous medium, caused by the thermal softening of the raw material. There should be a good correlation between the temperature range at which the reaction occurs and the softening point of the raw material, so that the gas remains blocked in the form of bubbles in the viscous mass. By cooling, a porous and homogeneous structure is formed, which constitutes the cellular glass. Of course, depending on many functional parameters and features of the raw material and added materials, the physical, mechanical and morphological characteristics of the cellular glass can vary [9].

The foaming agent adopted in the experiments presented in the paper was calcium carbonate. The reaction which releases the gas that contributes to the foaming process is:

$$CaCO_3 = CaO + CO_2 \quad (1)$$

The reaction (1) occurs at over 800 ºC. Calcium oxide (CaO) resulted during the carbonate decomposition enters in the starting material composition [9].

The same 0.8 kW domestic microwave oven (Figure 1) adapted for high temperature operation (above 1200 C) described in previously published own works [10] was used in this experiment. Also, the same technical solution for protecting the pressed powder mixture of the raw material with a ceramic tube made of a high microwave-susceptible material was adopted to reduce the effect of the direct impact of the microwave field on the glass-based material.

Figure 1. The experimental 0.8 kW-microwave oven

The thickness of the ceramic tube was 2.5 mm, which ensures a predominant penetration of the protective wall by the electromagnetic waves, but also a partial absorption of them in the wall mass. Thus, a mixed microwave heating is performed, both directly initiated in the core of the material by converting the radiation of the waves into heat [11, 12] and indirectly by the conventional thermal radiation. A very important role is played by the high thermal protection of the hot zone (the material subjected to heating and the ceramic tube including its lid made of the same ceramic material) in order to avoid heat loss outside the system.

The process temperature control was performed with a radiation pyrometer mounted above the furnace at about 400 mm, which can visualize the hot surface of the material through holes provided in the upper wall of the oven and the lid of the ceramic tube.

2.2 Materials

The basic raw materials used in experiments were blast furnace slag granulated by water cooling from the Arcelor Mittal Galati plant and colored glass waste (green and amber in equal proportions) recycled from post-consumer container glass. The chemical composition of the blast furnace slag included 37.66% SiO_2; 9.42% Al_2O_3; 45.41% CaO; 0.38% Fe_2O_3; 4.94% MgO; 0.42% Na_2O; 1.75% K_2O. The colored glass waste had the chemical composition [13] presented in Table 1.

The granulated blast furnace slag was ground in a ball mill and sieved, the grain size of the slag being below 63 μm. The glass waste was crushed and ground in the ball mill being used in experiments the fraction below 63 μm. The weight ratio of the two main raw materials (blast furnace slag and glass waste) varied between 50/50 (variant 1) and 40/60 (variant 4).

The other materials that completed the composition of the powder mixture were: calcium carbonate as a foaming agent, borax as a fluxing agent, titanium oxide as a nucleating agent, sodium phosphate as a foaming stabilizer and water addition as a binder.

The foaming agent ($CaCO_3$) was used in the range of 5.0-6.5 wt.%. The weight ratio of fluxing agent (borax) varied in a limited range of 7.8-8.1%. As the composition of the blast furnace slag does not contain TiO_2, it was necessary to add (5 wt.%) titanium oxides, which facilitates the nucleation of the glass-based raw material for glass-ceramic production. Sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) was used in a constant weight proportion of 3% The water addition as a binder for pressing the powder mixture was kept at the value of 8 wt.%.

Four experimental variants were adopted using the materials and additives mentioned above. Table 2 shows the experimental variants composition.

2.3 Characterization of the cellular glass samples

The cellular glass samples made by the sintering process of blast furnace slag and glass waste were characterized in laboratory. The apparent density was measured by the gravimetric method [14]. The porosity was calculated by the comparison method of the density of the compact material (melted and cooled) and the density of the porous material, experimentally measured [15]. The determination of the thermal conductivity was carried out by measuring the thermal flow that passes through the sample mass with a thickness of 50 mm placed between two metal plates. One plate was heated and protected with a thermal insulation and the other plate was cooled. The water permeability of the cellular glass was measured by the method of immersion of the sample in water (ASTM D 570). To determine the compressive strength of the porous material an device was used to develop an axial pressing force with a hydraulically operated piston. The sample had a cylindrical shape with the diameter of 80 mm and the height of 70 mm. The last pressing force axially applied to the sample before to crack was considered the compressive strength value. The microstructural configuration of the samples was performed with a Smartphone Digital Microscope. The crystallographic structure was investigated with the X-ray diffraction method (XRD), according to the standard EN 13925-2:

2003, using a X-ray diffractometer Bruker-AXS D8 Advance with CuKα radiation.

Table 1. The colored glass waste chemical composition (wt.%)

Glass waste type	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	Cr_2O_3	SO_3
Green	71.8	1.9	11.8	-	1.2	13.1	0.1	0.09	-
Amber	71.1	2.0	12.1	0.2	1.1	13.3	0.1	-	0.05

Table 2. Composition of the experimental variants (wt.%)

Variant	Colored glass waste	Blast furnace slag	$CaCO_3$	Borax	TiO_2	$Na_3PO_4 \cdot 12H_2O$	Water addition
1	39.25 (50)	39.25 (50)	5.0	8.1	5.0	3.0	8.0
2	41.45 (53)	36.75 (47)	5.5	8.0	5.0	3.0	8.0
3	44.40 (57)	33.50 (43)	6.0	7.9	5.0	3.0	8.0
4	46.50 (60)	31.00 (40)	6.5	7.8	5.0	3.0	8.0

3. RESULTS AND DISCUSSION

3.1 Results

As mentioned above, the experiments were performed on the 0.8 kW-microwave oven adapted for high temperature operation.

The main functional parameters of the manufacturing process of cellular glass presented in Table 3 include the dry raw material and additives amount, the foaming temperature, the heating time, the heating and cooling rate, index of volume growth, the cellular glass amount and the specific energy consumption.

The physical, mechanical and morphological characteristics of the cellular glass (apparent density, porosity, thermal conductivity, compressive strength, water absorption and pore size) are presented in Table 4.

Table 3. Main functional parameters of the manufacturing process of the cellular glass

Variant	Dry raw material/cellular glass amount g	Foaming temperature °C	Heating time min	Average rate, °C/min		Index of volume growth	Specific energy consumption kWh/kg
				Heating	Cooling		
1	560/ 538	905	44	20.11	6.1	2.20	0.95
2	560/ 536	903	43	20.53	5.8	2.10	0.94
3	560/ 540	901	42	20.98	6.0	1.95	0.91
4	560/ 539	900	41.5	21.20	5.8	1.80	0.90

Table 4. Physical, mechanical and morphological characteristics of the cellular glass samples

Variant	Apparent density g/cm^3	Porosity %	Thermal conductivity W/m·K	Compressive strength MPa	Water absorption %	Pore size mm
1	0.77	77.4	0.124	12.9	3.6	1.1 – 1.5
2	0.79	76.8	0.128	13.3	3.6	0.8 – 1.2
3	0.81	76.2	0.133	13.6	3.3	0.6 – 0.8
4	0.82	75.9	0.135	14.1	3.4	0.3 – 0.6

According to the data in Table 3, the final temperature of the sintering-foaming process of blast furnace slag and glass waste was around 900 °C (maximum 905 °C in the case of $CaCO_3$ proportion of 5.0 wt.%). The energy efficiency of the mixed microwave heating (predominantly direct) was highlighted by the high heating rate (20.11-21.20 °C/min) compared to the heating rates used in conventional processes (about 10 °C/min). Consequently, the specific energy consumption of the process had very low values (0.90-0.95 kWh/kg) being influenced only by the final temperature of the process and implicitly, by its duration.

Table 4 shows that the main physical, mechanical and morphological characteristics of the cellular glass samples obtained by rapid microwave heating were kept almost similar to those manufactured by conventional techniques (apparent density 0.77-0.82 g/cm^3, porosity 75.9-77.4%, thermal conductivity 0.124-0.135 W/m·K, water absorption 3.4-3.6%). Due to the influence of borax (due to its high boron content), TiO_2 (for the contribution to the crystallization of the raw material) and because the sintered and foamed material is a cellular glass-ceramic with a partially microcrystalline structure, the compressive strength of the samples was significantly higher (12.9-14.1 MPa) than in the case of ordinary cellular glasses and approximately at the level of samples achieved by conventional techniques and presented in the literature.

Images of the four cellular glass samples are shown in Figure 2 and pictures of the samples microstructure are presented in Figure 3.

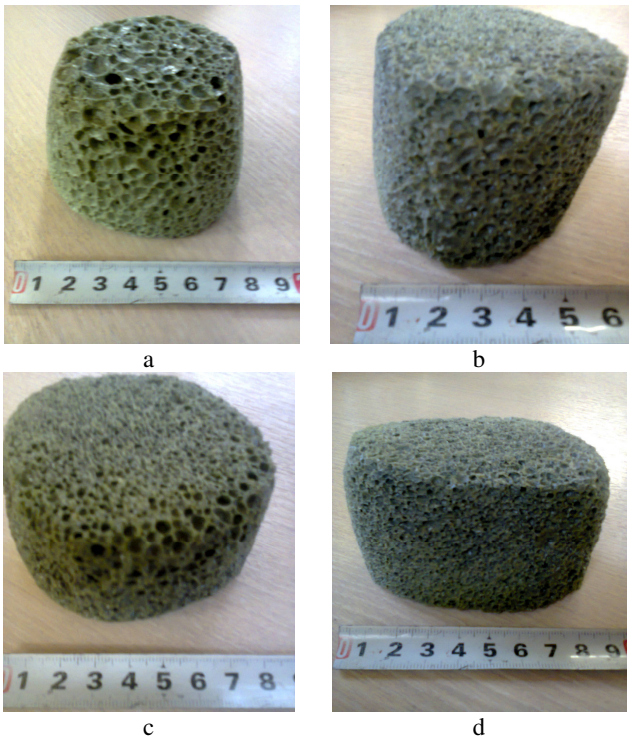
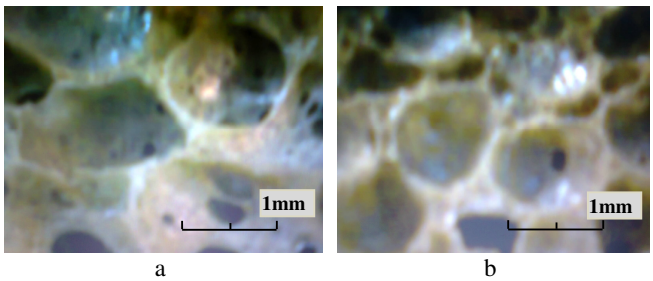
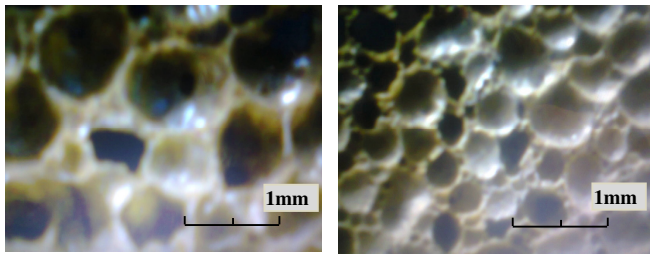


Figure 2. Pictures of the cellular glass samples
a – sample1, heated at 905 ºC; b – sample 2, heated at 903 ºC; c – sample 3, heated at 901 ºC; d – sample 4, heated at 900 ºC.



a b



c d

Figure 3. Pictures of the samples microstructure
a – sample 1; b – sample 2; c – sample 3; d – sample 4.

According to the two figures, the cellular glass sample with the finest and most homogeneous microstructure (pore size between 0.3-0.6 mm) was that corresponding to variant 4, produced from a blast furnace slag and glass waste ratio of 40/60, the most weight proportion of $CaCO_3$ (6.5%), 7.8% borax, 5% TiO_2 and 3% $Na_3PO_4 \cdot 12H_2O$.

The crystallographic structure of the cellular glass samples revealed the existence of a main phase (diopside) and to a lesser extent two other crystalline phases (augite and titanite) in all the analyzed samples.

3.2 Discussion

The production of cellular glass with high mechanical strength using the microwave energy should be analyzed on two directions: on the one hand, the physical, mechanical and morphological characteristics of the cellular glass samples and, on the other hand, the energy efficiency of the manufacturing process. Compared to the results presented in [2, 4], in which a titanium-rich blast furnace slag (20-27% TiO_2) was used as raw material and a cellular product was obtained whose compressive strength value reached even 25 MPa, the current paper had a blast furnace slag from Arcelor Mittal Galati with a chemical composition free of TiO_2. Under these conditions, an addition of TiO_2 was necessary to favor the nucleation and implicitly, the crystallization of the raw material.

The energy efficiency of the manufacturing process using microwave energy was remarkable obtaining very low values (0.90-0.95 kWh/kg), although a direct comparison with similar manufacturing processes by conventional methods was not possible because the literature does not provide this information. Theoretically, the conventional methods of heat treatment at 900 ºC of a mixture of blast furnace slag and soda-lime glass waste (50/50) cannot have a specific energy consumption below 1.38 kWh/kg, i.e. much more than that achieved by the nonconventional technique specified above.

4. CONCLUSION

The research aimed to produce a relatively lightweight cellular material with very high mechanical strength for construction applications obtained from recycled industrial and commercial waste (blast furnace slag and container glass waste) using the microwave energy, more efficient than the conventional energy.

Unlike the conventional energy used worldwide in the manufacturing process of cellular glass, the application of the microwave energy in similar processes allowed to obtain very low specific energy consumptions (0.90-0.95 kWh/kg).

A manufacturing recipe almost similar with some recipes presented in the literature, containing blast furnace slag and waste glass as raw material, $CaCO_3$ as a foaming agent, borax as a fluxing agent, TiO_2 as a nucleating agent, sodium phosphate as a foaming stabilizer and water addition as a binder, was used.

The best cellular glass sample was manufactured in the 0.8 kW-microwave oven from blast furnace slag and glass waste in the weight ratio of 40/60, 6.5% $CaCO_3$, 7.8% borax, 5% TiO_2, 3% sodium phosphate and 8% water addition by heat treatment at 900 ºC with the heating rate of 21.2 ºC/min. The apparent density was 0.82 g/cm^3, porosity - 75.9%, thermal conductivity - 0.135 W/m·K, compressive strength - 14.1 MPa, water absorption - 3.4% and pore size between 0.3-0.6 mm.

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