EXPANDED GLASS EXPERIMENTALLY MADE FROM RESIDUAL GLASS, ALUMINUM NITRIDE, AND MANGANESE DIOXIDE THROUGH MICROWAVE IRRADIATION HEATING

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ABSTRACT: An expanding agent (aluminum nitride) from the carbide and nitride group, less used in the cellular glass manufacturing process, was tested together with manganese dioxide in the experiment presented in the paper. The powder mixture of recycled residual glass and the two mentioned additives was thermally sintered and expanded by predominantly direct microwave irradiation at temperatures between 820-850 ºC. The remarkable energy efficiency of the original heating technique allowed obtaining very economic specific energy consumptions between 0.80-0.95 kWh/kg. The optimal products had the apparent density between 0.35-0.43 g cm^{-3}, porosity between 79.5-83.3 %, heat conductivity between 0.080-0.094 W $(mK)^{-1}$, and compression strength in the range 4.0-6.7 MPa. The cellular material has the characteristics required for its using as a thermal insulation material in the building sector.
KEYWORDS: cellular glass, residual glass, aluminium nitride, manganese dioxide, microwave heating.

1. INTRODUCTION

Climate overheating due to pollution and the energy crisis of the last decades have changed the attitude of mankind towards the waste regime generated worldwide as a result of industrial and domestic activities. Waste recycling has become a major concern of countries around the world, with regulations at the national, regional, and continental levels. The main types of waste are targeted: metals, plastics, glass, paper and cardboard, textiles, etc.

Glass is one of waste with the highest annual generation rate due to its relatively short lifespan. The main sources of waste glass in the world are consumed commercial beverage bottles and clear flat glass from the demolition and rehabilitation of civil constructions. Generally, the glass industry recycles residual glass, but prefers to recover the own waste resulting from its industrial manufacturing process, avoiding the high additional costs required to select the waste by color.

According to the data of The European Container Glass Federation (FEVE) [1], above 12 million tons of container glasses were collected and recycled in EU in 2019 with an average rate of recycled glass of 74 %.

In the last 3-4 decades, the recycling of residual glass for use as a basic material in the manufacture of cellular glass has attracted the interest of several industrial manufacturers in the United States and Europe. Glass has the peculiarity of keeping its physical-mechanical properties almost intact, the chemical and physical stability being remarkable. Given this peculiarity, it was discovered 80-90 years ago that glass waste could be used to produce a suitable thermal insulation material for building following a thermal expansion process [2]. By expanding, the glass becomes porous, lightweight, and with an excellent heat conductivity. In addition, due to the characteristics of the parental glass, the product has an acceptable mechanical resistance, is resistant to fire and moisture, anticorrosive, resistant to frost and aggression of insects, rodents, bacteria, etc., non-deformable, non-toxic, being a material made from waste that competes with other thermal insulation materials on the market (expanded polystyrene and extruded polystyrene) [3, 4].

The process of expanding the glass-based powder material takes place due to a chemical reaction of the expanding agent releasing a gas scattered in the thermally softened mass of the material forming numerous gas bubbles. Further increasing the process temperature leads to increase the gas pressure inside the bubbles and the glass expansion. The expanding agents commonly used in the industrial production are solid or liquid carbonaceous materials (coal, black carbon, silicon carbide, glycerol, etc.), and carbonates (most often calcium carbonate). Materials in the first category are prone to oxidation, while carbonates decompose, both types of reaction leading to the formation of

gaseous oxides (CO_2 or CO) that facilitate the expansion process [2]. Numerous other types of mineral expanding agents including also organic and vegetable agents (silicon nitride, sodium carbonate, dolomite, aluminum nitride, sodium hydroxide, coal fly ash, manganese dioxide, egg shell, clam shell, banana leaves, oak leaves, etc.) have been experimentally tested in cellular glass manufacturing processes in recent years.

The current work focused on commercial container glass foaming processes using aluminum nitride (AlN) as an expanding agent. The literature presents several data on small-scale experiments in the manufacture of cellular glass with this type of expanding agent. According to [5], glass industrial waste was heat treated at temperatures between 800-850 ºC with a maximum of 900 ºC, AlN (between 1.5-3 %) being used as an expanding agent and alternatively TiO_2 and steel making dust (mainly Fe_2O_3) as oxygen-supplying agents. The experiment performed on an electric oven demonstrated that the oxygen-supplying agents added leads to changes in closed porosity (specific to foaming without TiO_2 and/or Fe_2O_3) causing open porosity in fairly high proportions, especially as the process temperature increases. The apparent density of the expanded product is high (1.18 g cm^{-3}) in the case of heat treatment at a minimum temperature of 800 ºC using only AlN (2 %) without additives and decreases to 0.49 g cm^{-3} by increasing the temperature to 850 ºC and forming a structures with open porosities (64 %). By the addition of TiO_2 and Fe_2O_3 in the conditions of the structure with open porosities of over 75 % and the process temperature of 850 ºC, the apparent density decreases up to 0.41 g cm^{-3}. The lowest density value of the foamed product (0.29 g cm^{-3}) was obtained by using 3 % AlN and 6 % TiO_2 at 900 ºC, the open porosity being the highest (86 %).

According to the results published in [6], the residual glass recovered from the industrial polishing process of soda-lime glass was subjected to experimental expansion using very fine AlN powder at temperatures between 850-950 ºC. The weight ratio of the expanding agent which varied between 2.5-7.5 % and also the adopted sintering temperature influenced the sintering/foaming process. The bulk density of the expanded product was below 0.5 g cm^{-3}, the heat conductivity had relatively low values (between 0.090-0.106 W m^{-1} K^{-1}) and the compression strength varied between 0.65-2.48 MPa, the upper limits of conductivity and mechanical strength being reached at the highest values of the product density corresponding to the ratio of 2.5 % AlN. The highest values of the compression strength were obtained by sintering at 900 ºC (2.5 MPa corresponding to 2.5 % AlN, 1.5 MPa for 5 % AlN, and 1.6 MPa for 7.5 % AlN). Also, for the sintering temperature of 850 ºC the compression strength values were fairly high between 1.4-1.8 MPa corresponding to 7.5 % and 2.5 % AlN, respectively. Sintering at 950 ºC negatively influenced the mechanical strength of products (under 0.8 MPa). The pore size was small, the values being between 0.10-0.55 mm (the lowest value was reached at 950 ºC for 5 % AlN and the highest value at 850 ºC for the same AlN ratio). Based on the experimental results, it was considered that a wide range of cellular glass-ceramics can be obtained the products being suitable for various structural applications.

The use of AlN as an expanding agent with the addition of borax (sodium borate) as a flux agent to obtain cellular glass-ceramics by sintering at 1000 ºC of the mixture of residual glass powder and blast furnace slag with high-titanium content is presented in [7]. The weight ratio of AlN was varied between 1-5 % following the influence on the properties, microstructure and crystalline phases of the cellular product. It has been observed that the use of 3 % AlN has significantly changed the characteristics of the product. Thus, the porosity and pore size increased to this limit of the AlN proportion, after which they decreased. Instead, bulk density and compression strength decreased to minimum values corresponding to 3 % AlN and increased for 5 % AlN. The optimal properties of the cellular product were obtained in the case of 4 % AlN (density of 0.8 g cm^{-3}, porosity of 69 %, and compression resistance of 2.8 MPa).

The makers of this paper have conducted several small-scale experiments in the last 4-5 years in the domain of cellular glass making from residual glass using the nonconventional technique of thermal treatment of glass-based material through microwave radiation. In the world, all industrial processes as well as those experimental are performed by conventional methods. The advanced technique of microwave heating is not a new technique, being known for over a century, but it has been industrially used only in drying or low temperature heating processes. Furthermore, in the case of heat treatment of glass, an innovative technical solution applied for the first time by the authors' team was necessary to obtain the structural homogeneity of the expanded product [8].

The aim of the current paper is to test the manufacture of cellular glass in the oxidizing atmosphere of the microwave oven by using residual

glass mixed with AlN as an expanding agent and manganese dioxide (MnO_2) as an oxygen-supplying agent. In technological terms, this manufacturing recipe is new.

2. METHODS AND MATERIALS

2.1 Methods

As mentioned above, the known principle of the forming process of a cellular material by the thermal foaming of the glass powder is the liberation of a gas or gaseous compound inside the hot mass of the glass in the range of an adequate temperature. In the case of using AlN as an expanding agent, the released gaseous compound is nitrogen dioxide (NO_2). According to [9], the powder AlN oxidation takes place in the range 550-1100 ºC. The addition of MnO_2 to the starting material mixture has the role of providing additional oxygen to the oxygen available in the oxidizing atmosphere in the oven. MnO_2 decomposes in a first stage at about 483 ºC with a peak at about 590 ºC resulting Mn_2O_3 as a solid phase, which further decomposes at 650 ºC with a peak at about 800 ºC resulting Mn_3O_4 also as a solid phase. Both decomposition reactions release oxygen as a gaseous phase [10]. The chemical reactions that characterize the foaming process with AlN and MnO_2 are shown below.

$$4MnO_2 = 2Mn_2O_3 + O_2 \quad (1)$$
$$6Mn_2O_3 = 4Mn_3O_4 + O_2 \quad (2)$$
$$2AlN + 3.5O_2 = Al_2O_3 + 2NO_2 \quad (3)$$

The solid phases resulting from the reactions (Mn_3O_4 and Al_2O_3) enter into the molten glass composition and NO_2 is released participating to the expansion process.

The experimental equipment is the same used in the previous tests performed by the authors on the joint experimental basis of Daily Sourcing & Research SRL and Cosfel Action SRL, i.e. an 800 W-microwave oven of the type used in the household for food preparation modified for high temperature operation (over 1000 ºC). The mixture of glass-based raw material including the expanding agent is freely deposited as a pressed material on a stainless steel plate placed on a metal support above the heat insulation bed from ceramic fiber mattresses at the bottom of the oven. The plant originality is the placement of a cylindrical ceramic tube high microwave susceptible of SiC and Si_3N_4 with a wall thickness of 2.5 mm provided with a ceramic lid placed on the thermal insulation bed. The ceramic tube insulates the pressed mixture from the microwave source from one of the side walls of the oven, so that the material heating is done predominantly direct and partially indirect [8]. A radiation pyrometer mounted above the oven with visualizing through the holes provided in the upper wall of oven and the ceramic lid allowed the temperature control of the heat treated material. Figure 1 presents images of the experimental plant.

a b c

Figure 1. Overall and details of the experimental plant
a – overall image; b – 800 W-microwave oven; c – ceramic tube.

2.2 Materials

The basic component of the starting material mixture was a recycled colorless post-consumer drinking bottle. Its processing contained the operations of washing, sorting, breaking, grinding in a ball mill, and sieving performed in the company Bilmetal Industries SRL Popesti-Leordeni, Ilfov. The grain size of the waste used in the experiment was below 100 μm. The chemical composition of the colorless residual glass is the following: 71.7 % SiO_2, 1.9 % Al_2O_3, 12.0 % CaO, 1.0 % MgO, 13.3 % Na_2O, 0.05 % Cr_2O_3, and 0.05 % all other oxides [11].

Exhibiting good thermal conductivity and heat expansion properties similar to different semiconductors, the ability of AlN powder for glass foaming processes by oxidizing at about 700 ºC is known. Commercially available, the particle size of the powder used in the experiment was under 60 μm.

Manganese oxide (MnO_2) was used in the starting material mixture as an oxygen-supplying agent. Commercially obtained at a granulation under 50 μm, it was used in the experiment without further processing.

2.3 Cellular glass characterization methods

Characterization methods of expanded products used in previous experiments were also applied in this work. The gravimetric method [12] was used to determine the apparent density and the method of comparing the "true" density with the apparent density [13] was used to calculate the porosity of the samples. The determination of heat conductivity was performed by the guarded-comparative-longitudinal heat flow method (ASTM E1225-04) and the TA.XTplus Texture analyzer was used to identify the compression strength. To measure the volumetric proportion of absorbed water in the material it was applied the method of sample immersion in water (for 24 hours). The appearance of microstructural features of cellular glass was examined with ASONA 100X Zoom Smartphone Digital Microscope. To identify the crystalline phases of the expanded products at different temperatures it was applied the X-ray diffraction technique (XRD) according to EN 13925-2:2003, using X-ray diffractometer Bruker-AXS D8 Advance with CuKα radiation. The measurements and determinations of the cellular glass sample characteristics were performed in Daily Sourcing & Research SRL as well as in University "Politehnica" of Bucharest and Metallurgical Research Institute Bucharest.

3. RESULTS AND DISCUSSION

3.1 Results

The mixture of component materials including residual glass, AlN as an expanding agent, MnO_2 as an oxygen-supplying agent, and water addition as a binder was prepared in four different dosages being pressed into a metal mold and then removed to be freely placed in the microwave oven for its sintering and foaming at different temperature values. The material dosages corresponding to the four manufacturing recipes are shown in Table 1.

Table 2 presents the functional parameter values of the experimental manufacturing process.

Table 1. The material dosages of the four recipes

Recipe	Colorless residual glass (wt. %)	AlN (wt. %)	MnO_2 (wt. %)	Water addition (wt. %)
1	96.0	1.8	2.2	12.0
2	94.8	1.9	3.3	12.0
3	93.9	2.0	4.1	12.0
4	93.0	2.1	5.0	12.0

Table 2. Functional parameters of the experimental process

Recipe	Dry raw material/cellular glass amount (g)	Sintering/ expanding temperature (ºC)	Heating time (min)	Average rate (ºC/min)		Index of volume increasing	Specific consumption of energy (kWh/kg)
				Heating	Cooling		
1	485/470	820	36	22.2	5.5	1.30	0.80
2	485/472	830	38	21.3	5.3	1.40	0.84
3	485/471	840	40	20.5	5.4	1.90	0.88
4	485/471	850	43	19.3	5.3	2.40	0.95

Analyzing the data in Table 2, it can observe the remarkable energy efficiency of the predominantly direct microwave heating technique applied in the experiment presented above. The heating rate reached high values (between 19.3-22.2 ºC/min) by comparison with the heating speeds of the conventional procedures. By default, the specific energy consumption of the process had very economical values (below 0.95 kWh/kg), approximately at the average level of energy consumption specific to conventional industrial processes with continuous operation. According to [14], the transition from a small-scale microwave heating process to a similar industrial-scale process should allow an increase of energy efficiency up to 25 %. On the other hand, the combination of AlN as an expanding agent and MnO_2 as an oxygen-supplying agent used in this experiment proved to be very effective for the foaming process of glass.

The appearance of the four cross-section cellular glass samples obtained by microwave heating at temperatures between 820-850 ºC is shown in Figure 2.

According to the images in Figure 2, the samples obtained by sintering at lower temperatures (820 and 830 ºC) have fine porosity, while those produced at temperatures of 840 and 850 ºC have higher pore

size influencing their physical, thermal and mechanical characteristics.

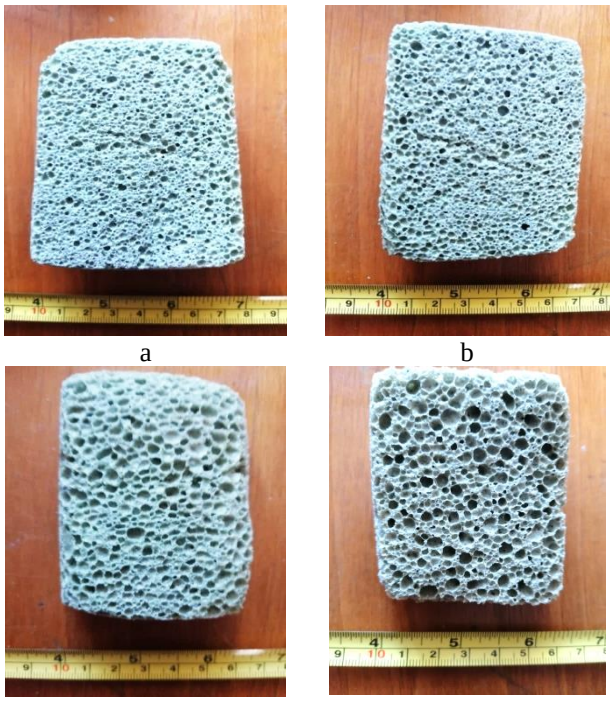

Figure 2. Appearance of the cross-section cellular glass samples
a – recipe 1; b – recipe 2; c – recipe 3; d – recipe 4.

Using the characterization methods of expanded products mentioned above, these features were identified the results being shown in Table 3.

Table 3. Features of the cellular glass samples

Feature	Recipe			
	1	2	3	4
Apparent density (g cm^{-3})	0.55	0.43	0.35	0.27
Porosity (%)	73.8	79.5	83.3	87.1
Heat conductivity (W $m^{-1}K^{-1}$)	0.125	0.094	0.080	0,075
Compression strength (MPa)	7.3	6.7	4.0	2.6
Water absorption (vol. %)	2.8	2.6	2.1	1.9
Pore dimension (mm)	0.1-0.4	0.3-0.9	0.8-1.2	1.2-2.0

The contribution of increasing the proportion of AlN from 1.8 to 2.1 wt. % and MnO_2 from 2.2 to 5.0 wt. % in the starting mixture on the physical, thermal, and mechanical properties of the cellular glass samples is evident according to the data in Table 3. Thus, the material becomes less dense (the apparent density decreases from 0.55 to 0.27 g cm^{-3} and the porosity increases from 73.8 to 87.1 %). Decreasing the apparent density values has the effect of reducing the heat conductivity values from 0.125 to 0.075 W $(mK)^{-1}$ and also reducing the compression strength values from 7.3 to 2.6 MPa.

The investigation of the microstructure appearance of the cellular glass samples shown in Figure 3 is also necessary.

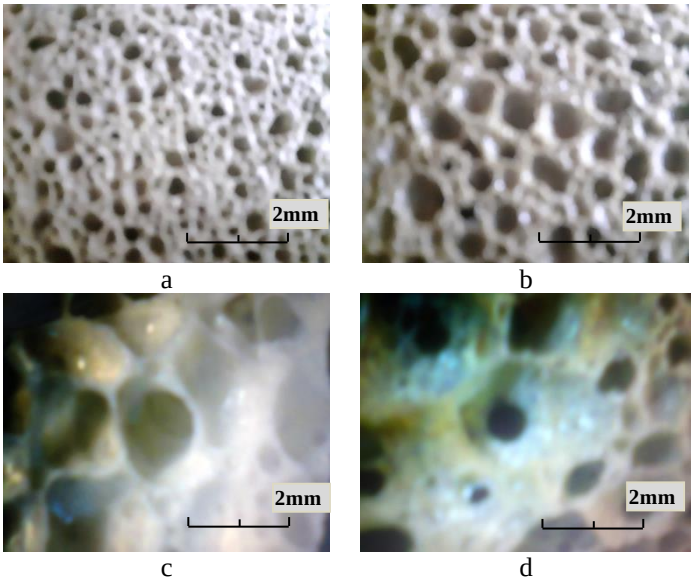

Figure 3. Images of the cellular glass sample microstructures
a – recipe 1; b – recipe 2; c – recipe 3; d – recipe 4.

The pictures above show the uniform distribution of pores in the microstructure of the four samples of cellular material. The pore size could be identified, the values being included in Table 3. If the first three samples are characterized by the existence of closed cells, which ensure a homogeneous thermal insulation of the material on the entire surface, the fourth has partially open cells with communication through walls with neighboring cells. This microstructural feature is not adequate to homogeneous thermal insulation.

The crystallographic analysis of cellular glass samples indicated the existence of two main crystalline phases: cristobalite (1) and AlN (aluminum nitride) (2). The XRD analysis is shown in Figure 4.

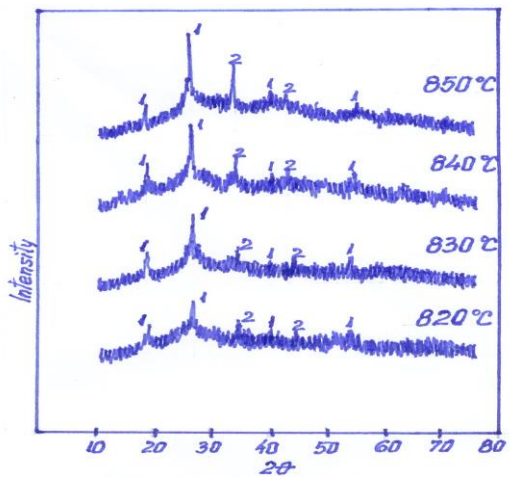

Figure 4. The XRD analysis

3.2 Discussion

The use of a wide proportions range of the expanding agent (AlN) and the oxygen-supplying agent (MnO_2) has led to the production of cellular products with a wide variety of physical, thermal, mechanical and morphological characteristics. The aim of the work was to produce a material with very good thermal insulation properties (low apparent density, high porosity, and low heat conductivity) and relatively high mechanical strength. The samples obtained with manufacturing recipes 1 and 4 have some extreme characteristics. Thus, sample 1 has high compression strength, but the apparent density and heat conductivity are quite high. Sample 4 has a low apparent density, but this characteristic is obtained by creating intercommunication channels between cells due to the semi-closed microstructure. For these reasons, samples 1 and 4 were not considered attractive. The choice of the optimal variant between samples 2 and 3 is difficult to make because both have characteristics located in ranges of acceptable values in terms of quality, so the authors have chosen to adopt both variants as optimal.

4. CONCLUSION

The use of AlN as an expanding agent together with MnO_2 and the application of the original technique of predominantly direct microwave heating have proven to be viable solutions for obtaining energy efficient cellular glass with thermal insulation properties (density between 0.35-0.43 g cm^{-3} and heat conductivity between 0.080-0.094 $W(mK)^{-1}$) and compression strength between 4.0-6.7 MPa suitable for the building sector.

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