

CELLULAR GLASS MADE OF CATHODE RAY TUBE GLASS WASTE IN MICROWAVE FIELD

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ABSTRACT: The paper presents a microwave based-nonconventional technique of manufacturing a cellular glass obtained by a heat treatment at 803 C of a powder mixture composed of glass waste from cathode ray tube (93 wt.%), MnO₂ (7 wt.%) as a foaming agent and water addition (10 wt.%). The cellular glass has excellent characteristics as an insulating material: apparent density of 0.19 g/cm³, porosity of 91.4%, thermal conductivity of 0.043 W/m·K and an acceptable compressive strength of 1.17 MPa. An economical specific energy consumption (1.16 kWh/kg) was obtained.

KEYWORDS: cellular glass, microwave reactor, CRT glass waste, manganese oxide, insulating material.

1. INTRODUCTION

Glass waste from technologically obsolete TV receivers in recent decades has become an important reserve available for recycling and, at the same time, hazardous waste included in the category of electrical and electronic waste [1]. A high content of lead oxide (16-25 wt.%) incorporated in the funnel glass of the cathode ray tube (CRT) is the main source of hazard. Also, the neck (the back part of CRT) is a lead-rich silicate glass containing up to 40% lead oxide, but the weight ratio of the neck is very low. The glass panel of the CRT has a very low content (less than 1 wt.%) of lead oxide and, at the same time, has the highest weight ratio (66 wt.%) of the three component parts of the CRT. Worldwide, the amount of waste represented by technologically obsolete TV receivers could be 2.4 million tons in 2020, according to the EU document [1]. The bibliographic source [2] considers that the recycling of CRT glass waste involves previous operations of removing the fluorescent powders, metal masks and implosion band, breaking and sorting (by sieving and handpicking) the waste. Through these processing operations, the initial amount of waste is reduced by 45% and the lead content could be decreased up to below 2000 ppm. The CRT glass waste is suitable for use as a raw material for the manufacture of cellular glass, floor tiles, bricks and concrete.

Although the industrial manufacturers of glass foams are not yet interested for the use of the CRT glass waste as a raw material, probably due to the requirement of an additional processing to remove the hazardous components compared to other available glass waste, numerous small-scale experimental results obtained by teams of

researchers worldwide are provided by the literature in the last decades.

A variant for the production of cellular glass in the form of pellets from CRT glass waste is presented in [3]. Sodium carbonate (Na₂CO₃) as a foaming agent was used in the weight ratio of 14%. The pellets obtained by firing at 750 °C, had a bulk density of 0.28 g/cm³.

Another paper [4] used calcium carbonate (CaCO₃) as a foaming agent. The sintering-foaming process of CRT glass waste occurred at 725 °C for 15-30 min. The cellular glass had an apparent density between 0.18-0.40 g/cm³ and a homogeneous porous structure with a pore size of 100 μm. At higher temperatures, the tendency to form an open cell microstructure was observed. The porosity of the cellular glass was 85% and the compressive strength had values up to 5 MPa.

A mixture of pelletized powders composed of CRT glass waste, dolomite (CaMg(CO₃)₂) and CaCO₃ as foaming agents, Na-bentonite and Ca-bentonite as pelletizing agents and a small addition of alumina (Al₂O₃) to avoid aggregation of the molten particles were sintered and foamed at 800 °C resulting foamed pellets (diameters of 4-6 mm) with the bulk density between 0.6-0.9 g/cm³ [5]. At temperatures slightly above 800 °C the tendency of the pores to communicate with each other was observed, partially forming a microstructure with open pores.

Other manufacturing recipes have included substitutes of CaCO₃ (egg shell waste or clam shell waste) as foaming agents in ratios of 5 wt.% and 2-10 wt.%, respectively [6, 7]. Processed together with the CRT glass waste at 700 °C they led to the production of pellets with the bulk density around 0.3 g/cm³.

A process of manufacturing cellular glass at 1050 °C from CRT glass waste using 4 wt.% silicon carbide (SiC) as foaming agent, 1.2 wt.% cobalt tetroxides (Co₃O₄) as oxygen supply agent to intensify the foaming process, water and polyvinyl alcohol as binders was presented in the paper [8]. The cellular glass had an apparent density of 0.60 g/cm³, porosity of 80%, flexural strength of 1.6 MPa and a fine microstructure with pore size below 1 mm.

According to [9], a foam product with the bulk density of 0.226 g/cm³, thermal conductivity of 0.68 W/m·K, flexural strength of 3.32 MPa and pore size between 0.5-0.9 mm was obtained at 880 °C for 30 min using CRT glass waste (56 wt.%) mixed with germanium tailing (40 wt.%), SiC (1 wt.%) as a foaming agent, sodium borate (borax) as a fluxing agent and titanium oxide (TiO₂) as a stabilizing agent.

Other information in the literature [10, 11] shows the use of SiC or titanium nitride (TiN) as alternative variants of reducing agents in the manufacturing process of glass foam from CRT glass waste. SiC or TiN reacts with lead oxide (PbO) in the composition of the glass waste releasing gases (CO₂ or N₂) that facilitate the foaming process.

The paper [12] presents results of the research conducted in the manufacture of a cellular glass from CRT panel glass waste using 1 wt.% borax as a fluxing agent, 1 wt.% TiO₂ as a stabilizing agent and 1-2.5 wt.% antimony trioxide (Sb₂O₃). The sintering-foaming temperature was 820 °C for 30 min. It was experimentally found that with increasing the Sb₂O₃ content in the above range, the density and compressive strength of the cellular glass tended to decrease. At the optimal ratio of Sb₂O₃ of 2.0 wt.%, the density was 0.19 g/cm³ and the compressive strength was 1.05 MPa.

In [13], a cellular glass was made from CRT panel glass waste (with a grain size below 32 μm) and manganese oxide (MnO₂) as a foaming agent (with a grain size below 40 μm). The proportion of MnO₂ was 7 wt.%, the remaining 93 wt.% representing the glass waste. The raw material was pelletized. The foaming heating process occurred at 790-810 °C for 5-160 min. The foamed pellets had the bulk density between 0.25-0.59 g/cm³, the porosity between 79-92% and the thermal conductivity in the range 0.053-0.066 W/m·K. The pore size varied between 0.02-4 mm. At temperatures higher than 800 °C, a slight tendency of the pores to join together was observed, forming a partially open microstructure and strongly influencing the compressive strength.

All experiments described in the literature and presented above were performed using conventional heating methods. An only paper [14] refers to the manufacture of cellular glass from CRT glass waste having as energy source, the microwave radiation (at a frequency of 12 GHz). The carbon (C) in proportions between 0.5-2 wt.% was used as a foaming agent for CRT glass waste, the density of the foamed material decreasing from 0.58 to 0.23 g/cm³ with the increase of the C proportion. In the same paper it is also described the use of a mixture of C, TiO₂, MnO and AlN in weight ratios of 1.5; 2; 4 and 2, respectively, the rest being the CRT glass waste. In this variant a very low density cellular glass (0.16 g/cm³) was obtained.

According to a very recent work [15], the research team of the current paper experimentally manufactured a cellular glass with very good insulating material properties (porosity of 90%, thermal conductivity of 0.042 W/m·K and compressive strength of 2.1 MPa) adequate for use in construction. The raw material was a CRT glass waste and the additives were CaCO₃, borax and Sb₂O₃. The heating technique was nonconventional demonstrating an excellent energy efficiency. The specific energy consumption was very low (0.72 kWh/kg) being more economical than that corresponding to the industrial manufacturing processes of glass foam.

Although known for over 85 years, the application of the microwave heating technique at high temperatures (over 700 °C) is still in its infancy. The microwave energy is industrially used only in drying processes or that require relatively low temperatures. According to [16], only in the last 10-15 years it has been experimentally found that several types of material (organics, ceramics, polymers, metals, glasses, etc.) are suitable for microwave heating, but generally, microwave energy-based processes are still in the experimental stage. In the last three years, a team of researchers from the Romanian company Daily Sourcing & Research has conducted numerous experiments related to the manufacture of cellular glass by applying the nonconventional technique and obtained promising results published in international and Romanian journals.

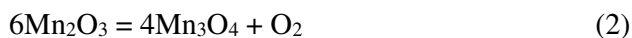
2. METHODS AND MATERIALS

2.1 Methods

Generally, the basic principle of the foaming process of glass waste is the release of a gas into the softened viscous mass of the raw material mixture forming a network of bubbles trapped in this mass. The gas comes from a chemical reaction of

oxidation, decomposition or reduction of a foaming agent. By cooling the material after stopping the heating process, a homogeneous porous structure is formed which constitutes the cellular glass (or glass foam) [4]. An essential condition is the correlation between the temperature at which the gas release reaction occurs and the softening temperature of the powder mixture. It is necessary that the viscosity of the mixture be adequate to block the gas bubbles. A too low viscosity does not allow the development of bubbles in the material mass, while a too high viscosity leads to the loss of gas bubbles, which will leave the material.

In the specific case of using MnO_2 as a foaming agent, the following thermal decomposition reactions occur [17]:



The reactions were studied by means of the thermal analyses (TG, DTA and DSC). The reaction (1) begins at about 583 °C and has a temperature peak of about 590 °C. The reaction (2) begins at about 650 °C and has the temperature peak at about 800 °C [17].

The equipment adopted for the experiments was a microwave reactor (Figure 1a) equipped with three microwave generators (each with a power of 1 kW) placed equidistantly on the side wall of the cylindrical cavity of the reactor. Inside the cavity is inserted a cylindrical crucible (Figure 1b) made of SiC with a wall thickness of 15 mm, an outer diameter of 180 mm and a height of 300 mm. The material from which the crucible is made is highly microwave susceptible. It completely absorbs the electromagnetic radiation, converts it into heat causing the rapid heating of the crucible wall. A very important characteristic of the heat process is the efficient thermal protection of the outer surface of the crucible to avoid the heat loss outside. Thick layers of ceramic fiber mattresses are pressed placed in the space between the crucible and the metal shell of the reactor cavity as well as at the base of the crucible. Inside the SiC crucible the pressed powder mixture of the raw material containing also the foaming agent is inserted. The pressing was previously performed in a metal mold using water as a binder. After pressing, the material is released from the mold and inserted freely into the crucible. The upper opening of the crucible is protected with ceramic fiber mattresses provided with an axial central hole with a diameter of 30 mm for viewing the surface of the heated material with a radiation pyrometer mounted above the reactor. The upper

area of the reactor is closed with a metal lid also provided with a central hole.

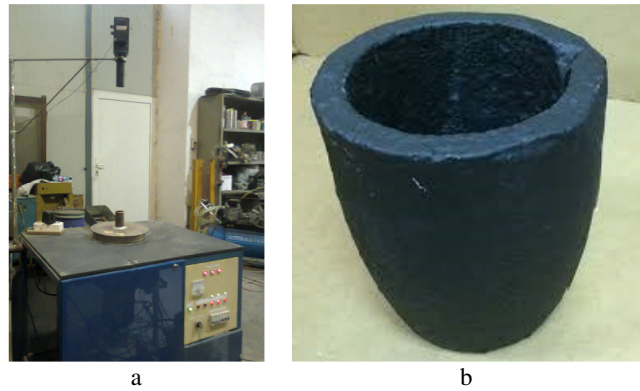


Figure 1. The microwave equipment

a – overall image of the equipment; b – silicon carbide-based crucible

Using a SiC crucible with a relatively large wall thickness, the microwave heating method is indirect, because the microwave field cannot penetrate the crucible wall, unlike other experiments performed with ceramic crucibles or tubes with a wall thickness below 5 mm, which allow the mixed microwave heating with higher energy efficiency. Using a crucible with a much larger useful volume than the crucibles with a small wall thickness, it was possible to heat a significantly larger amount of glass-based material.

2.2 Materials

The materials used in experiments were: recycled panel glass of CRT waste as raw material and MnO_2 as a foaming agent. The glass waste was crushed, ground in a ball mill and sieved, the grain size being below 32 μm . The chemical composition of the glass waste [13] was: 61.04% SiO_2 ; 2.37% Al_2O_3 ; 7.74% Na_2O ; 7.11% K_2O ; 0.32% MgO ; 0.84% CaO ; 7.82% SrO ; 9.66% BaO ; 1.52% ZrO_2 ; 0.34% TiO_2 ; 0.18% Fe_2O_3 ; 0.20% ZnO ; 0.23% PbO and 0.43% Sb_2O_3 . MnO_2 powder had a very low grain size below 20 μm [18]. Water was used as a binder.

2.3 Characterization of the cellular glass samples

The cellular glass samples produced by the sintering-foaming process of the CRT glass waste were characterized by traditional analysis methods. The apparent density was measured by the gravimetric method [19]. The porosity was calculated by the comparison method [20] between the porous sample density and the density of the same material type in compact state (melted and then cooled to room temperature). The determining method of the thermal conductivity [21] was the measurement of the thermal flow that crosses a sample of standard dimensions (50 mm-thickness) placed between two metal plates, one heated and

protected with insulating material and the other cooled. An axially press hydraulically operating was used to determine the compression strength. The water absorption of the cellular glass sample was measured by the traditional method of its water immersion (ASTM D 570). The microstructure of the samples was observed with a Smartphone Digital Microscope.

3. RESULTS AND DISCUSSION

Four experimental variants to produce cellular glass in the microwave reactor were adopted, being shown in Table 1.

The main functional parameters of the manufacturing process of cellular glass and the

physical, mechanical and morphological characteristics of the samples are shown in Tables 2 and 3.

Table 1. Composition of the experimental variants

Composition (wt.%)	Variant			
	1	2	3	4
CRT panel glass waste	93.5	93.0	92.5	92.0
MnO ₂	6.5	7.0	7.5	8.0
Water addition	10.0	10.0	10.0	10.0

Table 2. Main functional parameters of the manufacturing process of cellular glass

Variant	Dry raw material/cellular glass amount kg	Sintering-foaming temperature °C	Heating time min	Average speed, °C/min		Index of volume growth	Specific energy consumption kWh/kg
				Heating	Cooling		
1	1.70/ 1.66	798	43	18.1	6.9	1.9	1.12
2	1.70/ 1.65	803	44	17.8	6.7	2.3	1.16
3	1.70/ 1.64	807	46	17.1	7.0	2.5	1.22
4	1.70/ 1.65	810	50	15.8	6.9	2.7	1.31

Table 3. Physical, mechanical and morphological characteristics of the sample

Variant	Apparent density g/cm ³	Porosity %	Thermal conductivity W/m·K	Compressive strength MPa	Water absorption %	Pore size mm
1	0.21	90.5	0.046	1.19	0.8	0.1 – 0.4
2	0.19	91.4	0.043	1.17	0.8	0.2 – 0.6
3	0.20	90.9	0.046	1.13	1.2	0.4 – 0.8
4	0.18	91.8	0.042	1.09	2.5	0.8 – 1.3

Analyzing the data in Table 2, it can see the relatively large amount of raw material subjected to the sintering-foaming process compared to all previous experiments performed by the team of researchers from Daily Sourcing & Research. The 3 kW-microwave reactor was suitable for efficiently heating an amount of 1.70 kg of glass-based dry raw material.

According to the thermal analyses (TG, DTA and DSC) of the thermal decomposition reactions of MnO₂ and Mn₂O₃, the foaming process temperature was around 800 °C [17]. Experimentally, the process temperature was between 798-810 °C.

Although the microwave heating of the material was performed indirectly, the heating speed had high

enough values, reaching 18.1 °C/min in the case of the minimum proportion of MnO₂ (variant 1).

The index of volume growth had an acceptable level (1.9-2.7), the highest value corresponding to variant 4 with the maximum proportion of MnO₂ (8 wt.%).

The specific energy consumption had values between 1.12-1.31 kWh/kg being an economical consumption, although the previous values corresponding to the mixed microwave heating (partly direct, partly indirect) were around 0.80 kWh/kg.

The data in Table 3 show the qualitative performance of the cellular glass samples. Due to a previous high raw material processing, the apparent density of the samples was very low (0.18-0.21 g/cm³) for all four variants. Accordingly, the

porosity had very high values (over 90.5%) and the thermal conductivity had very low values (below 0.046 W/m·K). Instead, the compressive strength was low, with values below 1.19 MPa. The water absorption had low values, especially corresponding to samples 1 and 2 (less than 1%).

Pictures of the cross section of the four samples are shown in Figure 2.

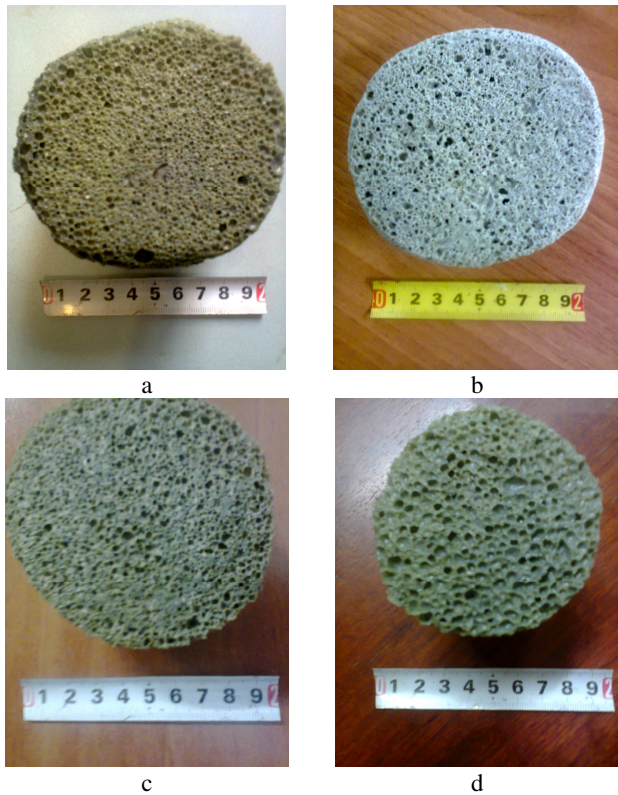


Figure 2. Pictures of the cross section of the samples
a – sample 1; b – sample 2; c – sample 3; d – sample 4.

According to Figure 2, the four cellular glass samples have a very fine porosity, the pore size increasing from sample 1 to sample 4, with the increase of the proportion of MnO₂ as a foaming agent.

The pore dimensions are clearly highlighted in the microstructure images of the samples in Figure 3.

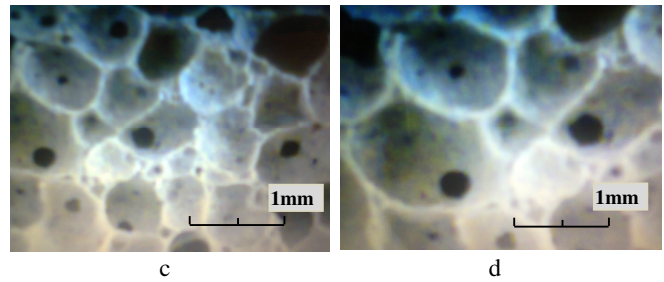
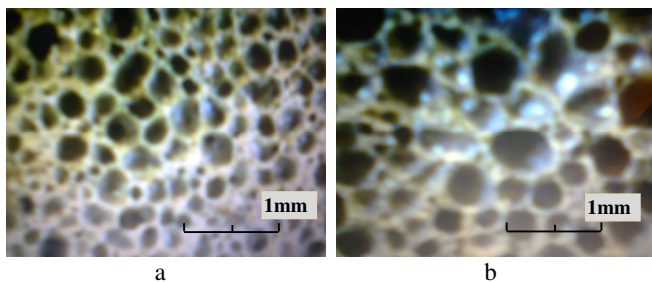


Figure 3. Pictures of the samples microstructure

a – sample 1; b – sample 2; c – sample 3; d – sample 4.

According also to the data in Table 3, the pore sizes vary from 0.1-0.4 mm corresponding to sample 1 to 0.8-1.3 mm corresponding to sample 4. It can be seen that the microstructures of samples 3 and 4 show the tendency to communicate with neighboring pores (especially, sample 4). This trend was observed in all foaming processes of CRT glass waste at temperatures generally, above 800 °C. Samples 3 and 4 had foaming temperatures of 807 and 810 °C, respectively. The influence of the microstructure transformation from one with closed pores, to one with partially open porosity, consists mainly in the decrease of the compressive strength.

Considering these observations, the optimal sample is sample 2 obtained by the heat treatment at 803 °C of the powder mixture consisting of CRT glass waste (93 wt.%), MnO₂ (7 wt.%) and water addition (10 wt.%). The cellular glass has an apparent density of 0.19 g/cm³, a porosity of 91.4%, a thermal conductivity of 0.043 W/m·K and a compressive strength of 1.17 MPa.

4. CONCLUSION

A cellular glass with excellent characteristics of insulating material was manufactured in a microwave reactor at 803 °C of cathode ray tube glass waste (93 wt.%), manganese oxide (7 wt.%) as a foaming agent and water addition (10 wt.%).

The cellular glass characteristics are: apparent density of 0.19 g/cm³, porosity of 91.4%, thermal conductivity of 0.043 W/m·K and an acceptable compressive strength of 1.17 MPa.

In experiments it was adopted the indirect microwave heating technique using a large silicon carbide crucible with thick wall (15 mm), which allowed to produce the greatest amount of cellular glass (1.65 kg).

An economical specific energy consumption (1.16 kWh/kg) was obtained.

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