

Glass Foams Containing Fly Ash And Sheet Glass By Adding Calcite As Foaming Agent

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Abstract

Glass foam is a porous isolation material used for heat isolation. In this study, the possibilities of glass foam production using calcite as a foaming agent was investigated. The mixture was prepared 10% wt. of waste window glass and 90% wt. Seyitömer thermal power plant fly ash. 2.5 to 10% wt. calcite was added to mixture and pressed under 75 MPa pressure by uniaxial cold pressing to obtain cylindrical specimens. Pressed samples sintered at 750-950 °C temperature range for 1 hour according to differential thermal analysis (DTA) results. The effect of calcite addition and sintering temperature on the porosity, density, compressive strength, microstructure and crystalline phases were investigated. It was determined that the

properties of glass foams was changing depend on calcite addition as foaming agent and the sintering temperature. The results showed that calcite provide foaming in specific proportions for glass foam production.

Keywords: Calcite, fly ash, glass powder, glass foam

1. INTRODUCTION

Calcite is an abundant rock-forming mineral in the Earth's upper crust. It is a carbonate mineral and the most stable polymorph of calcium carbonate (CaCO_3). It has a defining mohs hardness of 3, a specific gravity of 2.71, and its luster is vitreous in crystallized varieties. Color is white or none, though shades of gray, red, orange, yellow, green, blue, violet, brown, or even black can occur when the mineral is charged with impurities. The dissolution and precipitation behavior of calcite has been widely studied since it plays an important role in rock weathering and soil chemistry and therefore these processes impose controls on the natural sequestration of CO_2 . The carbon dioxide gas (CO_2) is given off as bubbles and the calcium dissolves in the calcinations reactions. Because of this features, some minerals including carbonate can be used for foaming process (Vavouraki 2008, Wikipedia 2012).

Foam glass is a porous heat-insulating and soundproof material, with true porosity up to 90 vol.%. Foam glass is a heterophase system consisting of the gaseous and the solid phases. The solid phase is glass that forms thin walls of single cells several micrometers thick. The cells are filled with the gaseous phase. These materials have many properties such as high surface area, high permeability, low density, low specific heat for high thermal and acoustic insulation and high chemical resistance. Glass foams are resistant to water and water vapor and do not burn. Commercial glass foams exhibit porosity, apparent density and compressive strength values of about 85–95 vol.%, 0.1–0.3 g/cm³ and 0.4–6 MPa, respectively (Fernandes 2009). Several synthesis routes are available to produce foam materials such as bubbles generation in slurries or in a green body during a specific thermal treatment, reaction sintering, sol–gel methods, direct foaming, pyrolysis of organic additives and polymeric sponge method (de Sousa 2008). There are a lot of investigations for production of glass foam materials. To investigate the effect of different additives and different raw materials on foaming process is popular issue, recently.

In the current study, the production possibilities of glass foam materials including sheet glass, fly ash and calcite were investigated. It is possible that this study can provide new view point for producibility of more economical glass foam material.

2. EXPERIMENTAL PROCEDURE

In the present study, cullet of commercially produced soda lime sheet (SLS) glass and power plant fly ash (Seyitömer-Turkey) were used as raw materials and their chemical analysis was performed by x-ray fluorescence (PHILIPS PW2404). The chemical compositions of fly ash and sheet glass were given in Table 1. and Table 2., respectively. Firstly, cullet glass was crushed and then dry milled using a ring mill (RETSCH). The main mixture was prepared fly ash 10 wt. % and sheet glass 90 wt. %. Calcite was added to mixture in the proportions of 2.5-10 % against sheet glass proportion in main mixture decreased by calcite addition for using more waste fly ash. Four different compositions were prepared from glass and fly ash with calcite addition by using ball mill for 1 h. The code schedule for samples was given in Table 3.

Table 1. Chemical composition of fly ash

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SO ₃	K ₂ O	TiO ₂	NiO	Na ₂ O	P ₂ O ₅	Cl	L.O.I
Wt. %	56.896	17.246	10.628	5.137	4.316	2.398	1.554	0.677	0.236	0.311	0.128	0.028	0.445

Table 2. Chemical composition of sheet glass

Oxide	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	Cl	K ₂ O	TiO ₂	Fe ₂ O ₃	SO ₃	L.O.I
%	73.195	9.916	8.590	5.998	1.515	0.025	0.108	0.040	0.185	0.338	0.09

Table 3. Sample code schedule

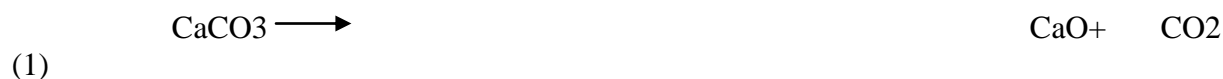
Sample code	Cullet (wt.%)	Fly ash(wt.%)	Calcite (wt.%)
25C	87.5	10	2.5
50C	85	10	5
75C	82.5	10	7.5
100C	80	10	10

In establishing an optimal heat treatment procedure for foam reduction the thermal behavior of glass cullet, fly ash and carbonates lays a key role. Differential thermal analysis (DTA) (SEIKO Exstar 6000) was used to determine glass transition and crystallization temperature for raw materials.

The cylindrically shaped samples with diameter of 25 mm and thickness of 15 mm obtained by uniaxial pressing (800 kg/cm²) were sintered between 750 °C and 950 °C for 1 h according to DTA results of sheet glass, fly ash and calcite. To characterize the prepared samples apparent density, porosity, compressive strength and visual observation were performed. Leica stereo microscopy was used for visual studies. X-ray diffraction analysis (XRD) was used for phase analysis and scanning electron microscopy (SEM, JEOL 6060) was carried out for microstructural investigations. X-ray diffraction analysis (XRD) using Rigaku type diffractometer with a CuK α radiation, which has a wavelength of 1.54056 Å to analyze phases present in the coatings over a 2 θ range of 10 $^{\circ}$ –90 $^{\circ}$ were used for characterization of the glass foam samples.

3. RESULT AND DISCUSSION

DTA results of raw materials used glass foam production are shown in Figure 1. Glass transition temperature was determined 550 °C for sheet glass (Figure 1a). Calcite exhibits a strong endothermic peaks corresponding to moments of weight loss (Figure 1b) characteristic of this material. The endothermic peak (790 °C) was due to the decomposition of calcium carbonate (calcite) with release of CO₂, according to the Eq. (1). The total weight loss was about 45%.



An exothermic peak in DTA analysis of fly ash was detected at 460 °C (Fig. 1c). Accordingly, the weight loss of 3.1% occurs at the same temperature. This exothermic peak occurs due to the unburned carbon reaction in fly ash. In this study sintering and foaming temperatures were selected according to DTA results shown in Figure 1.

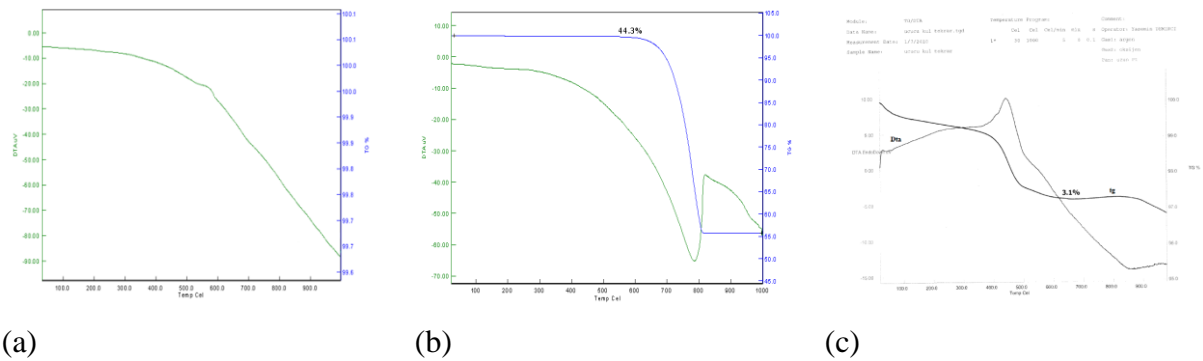


Figure 1. Thermal analysis (heating rate 5 °C/min) of (a) sheet glass, (b) calcite and (c) fly ash

Tridymite (ASTM chard no: 42-1401), Cristobalite (ASTM chard no: 82-0512), Diopside (ASTM chard no: 75-1092) and Augite (ASTM chard no: 78-1391) phases were determined by XRD analysis. Augite was determine in sample including calsite 10 % but not determined for the sample including calcite 2.5 %. The first significant point in XRD results is that peak intensities and numbers increase with increasing sintering temperature due to better crystallization. The intensities of Diopside and Augite peaks increase with increasing calcite addition and sintering temperature, clearly. The zone under the XRD patterns illustrates glass structure in body. The changing volumes of this zone infer to crystallization. When the sintering temperature was 950 °C, this zone got narrow, markedly. The effect of sintering temperature on crystallization is seen this way, clearly. Especially, Tridymite and Augite are characteristic phases for glass foam material in literature (Fernandes 2009).

After the sintering process, dimensional change test was performed for the samples. These results were given in Figure 2. It was shown that there are two important parameters influencing dimensional change. The first parameter is sintering temperature, the second is calcite addition. In general, dimensional change increases with increasing sintering temperature up to 900 °C. Above the this temperature, vitrification effect of liquid phase sintering mechanism cause firing shrinkage due to better sintering. Calcite addition has a positive effect on dimensional changes for calcite addition 2.5-5 %. When the calcite addition increased, dimensional changes decreased because of over gassing reactions. When the reaction between CaCO₃ and O₂ occurs, CaO and CO₂ gases form. Released gas provide softening and expansion for matrix. This mechanism is related to foaming process. When the foaming agent volumes increased excessively, gas pressure increases and the gas bubbles consisting of porosities explode due to high pressure. It is possible that the pressure of CO and CO₂ gases force glass matrix and thus, gas pores shrinkage happen (Hasheminia 2012). That the highest dimensional change value is 41.17 % was determined in calcite 5 % reinforced sample sintered at 900 °C. Calcite addition has negative effect on dimensional changes for some situation.

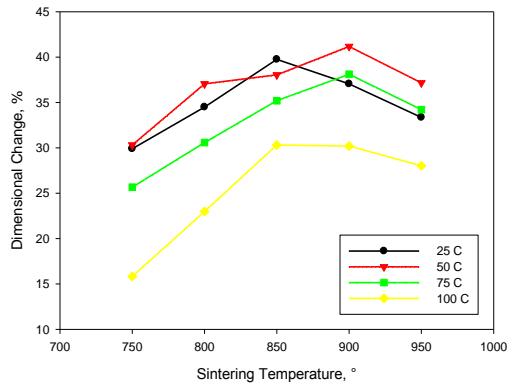


Figure 2. Dimensional test results versus sintering temperature

The macro photographs of samples can be seen in Figure 3. It is clear that dimensional changes and sintering temperatures increase in direct proportion. Increasing sintering temperature provide better sintering. The highest dimensional changes and the most foaming were observed in samples sintered at 900 and 950 °C. The samples including calcite 5 % were exposed to deformation. At 750-850 °C, pores and cracks on the surfaces formed due to the escaping gas from the decomposition of CaCO₃. This situation infers that gas pressures in these samples are maximum point. When it comes to other samples, the volume expanded and the surfaces became smooth with increasing temperature.

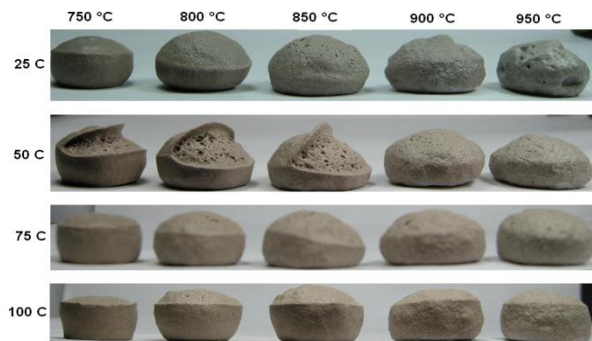


Figure 3. The macro photographs of samples

The curves of porosity values of the samples depending on sintering temperature are given in Figure 4a. Porosity values are correlation with dimensional change results. The highest porosity value was measured in coded 50 C sample sintered at 850 °C. The samples sintered at low temperatures have higher density and lower porosity due to the occurrence of a higher viscosity. The maximum porosity values in this study were calculated as 49.25 % in sample including calcite 5 % sintered at 850 °C. This value for commercial glass foam material is about 85-95 % (Scheffler 2005). The porosity values are correlation with macro photographs of samples. The samples containing higher calcite content have lower porosity values.

The density changes with sintering temperature are shown Figure 4b. The lowest density was measured as 0.43 gr/cm³ in 25 C coded samples sintered at 850 °C. The samples including calcite 5 % sintered at 800-850 °C have lowest density because of their pore structure. In these samples, pore size is not big compared to other groups but pore numbers are too much, comparatively. Density values in commercial glass foams are about 0.1-0.3 gr/cm³ (Scheffler 2005). Apparent density of the glass foam obtained from glass-calcite mixture is about 0.4-1 gr/cm³. The density increases with increasing calcite addition. Extensive calcite addition cause negative effect on foaming process. Higher sintering temperatures have similar effect on foaming and densities due to better sintering and lower viscosity.

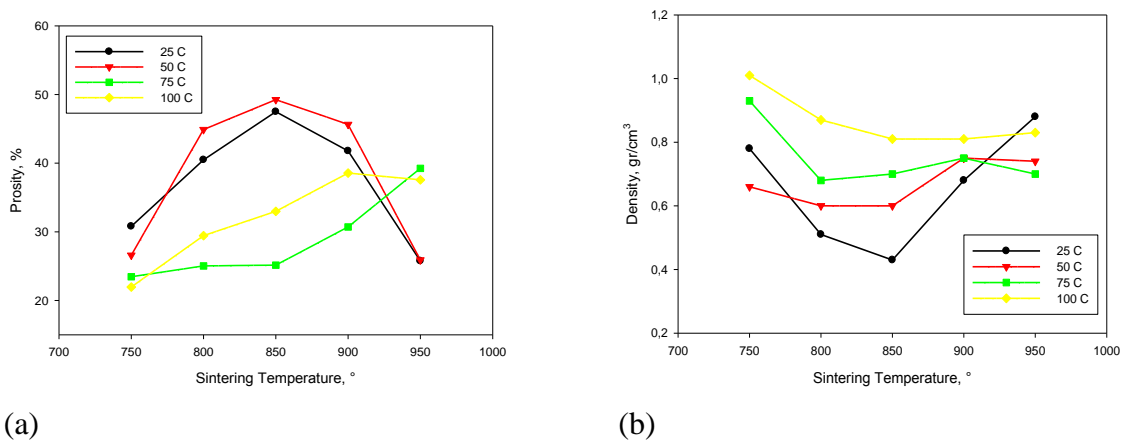


Figure 4. a) Porosities versus sintering temperature, b) Density values versus sintering temperature

The curves of compressive strength depending on sintering temperature were given in Figure 5. These results are correlation with porosity and density values. Porosity values are inversely proportional to the compressive strength. Compressive strength decreases with increasing the amount of porosity. The highest compressive strength values (4.75 MPa) are gained from the samples including calcite 10 %. In general, compressive strength decreases with increasing sintering temperature. Calcite addition has adverse effect compared to sintering temperature effect.

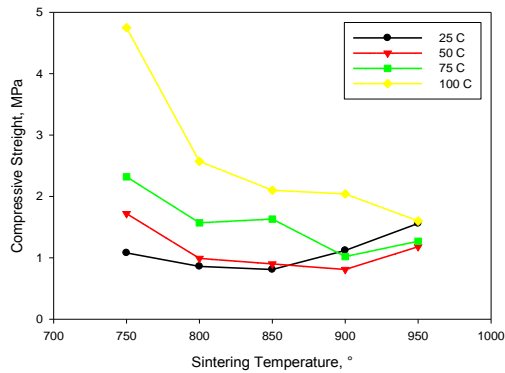


Figure 5. Compressive strength versus sintering temperature

Figure 6 shows the typical aspect of the glass foams of all the investigated compositions. The amount of calcite in the batch considerably affects the size and the shape of the pores. In general, the glass foam samples have inhomogeneous microstructures with irregular pores with a high scattering in their size (0.1–1 mm). Some pores were smaller than others, these pores were then sealed by the glassy phase when the sintering temperature increased due to the increasing viscosity. Since the addition of more calcite produced more gas, the pores became larger, suddenly. This situation is also observed in similar studies (Fernandes 2009, Bernardo 2007, Chong Liao 2012).

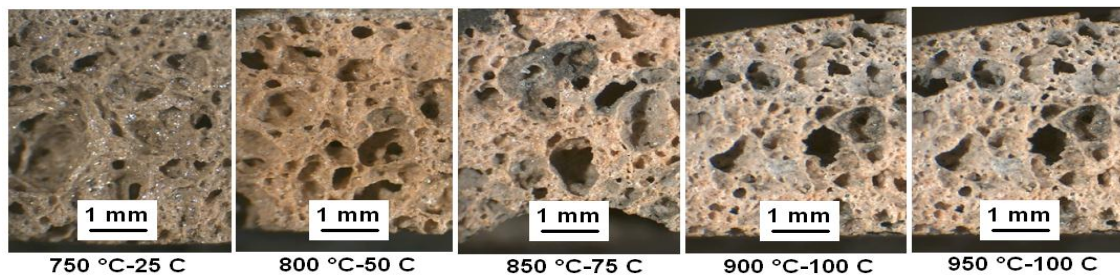


Figure 6. Stereo microscopy visions of samples of cross-section surface

4. CONCLUSION

XRD analysis showed that Tridymite, Cristobalite, Diopside and Augite crystalline phases formed in the glass foams. 49.25 % is the highest porosity value in coded 5C sample sintered at 850 °C. The lowest density 0.43 gr/cm³ was measured in coded 25C sample sintered at 850 °C. The porosity sizes increases with increasing sintering temperature. In the same time, calcite addition has a positive effect on foaming process in general. But calcite addition caused adverse effect on foaming process in some condition due to gas reactions. Micro and macrostructure analysis shown that the pore sizes and shapes are very irregular and the structures seem inhomogeneous.

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