Research Paper

Sintering of Glass - Steel Slag-SiC Composite as a Foam

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ABSTRACT

Foam glass-ceramics are porous material with the desired strength. In this work, steel slag was mixed with soda lime glass in (20, 40, 50, 60, 70 wt. %,denoted by SG20,SG40,SG50,SG60,SG70) and 5 wt.% SiC. Giving to Hot stage microscopy images, glass-slag composite's contraction starts at 1050ºC.
According to the SEM micrographs the tunnel-like pore porosity resulted from the decomposition of carbide phase were formed. The sizes of pors varies in 500 - 1000 μm range. More over by the 50 wt. % soda lime glass addition and sintering at 1200 ° C, the spherical porosity were formed and the size of the porosity were reduced to 50 μm in these composites. Also, by the the glassy phase increasing, the total porosity was increased to 80%, the density decreased to 0.8g / cm^{3}in SG40. This composite as a porous material has 2 to 5 MPa bending strengths. Wollastonite phase was detected in these composite.

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1. Introduction

Foam glass and glass -ceramics are one of the most important types of foams and materials, which are used in various applications such as road building, building and petrochemical industries, as thermal insulation, filters and fillers [1]. These materials have advantages such as chemical stability, flammability, high compressive strength, frost resistance and water vapor, suitable dimensional stability and resistance to living organisms such as moss and lichen as well as rodents [2-4]. Despite the advantages mentioned above, the most important defect in glass foam and ceramic glass is the high price of these products. To reduce the price, the most important solution is to replace the cheaper materials rather than the original glass. For this purpose, many researches have been carried out on the use of waste materials such as waste scrap, slag, ash from coal-fired power plants and municipal waste ash. Bernardo [5] in his studies which called them self glazed foam, used the waste glass and slag compositions. He concluded that the liquid phase resulted from the soft glass (glasses with low viscosity) could solve the waste minerals like amorphous slag. This dissolution causes the secondary crystallization of calcium silicate and aluminum silicate phases. So, the high iron oxide bearing slag is suitable to create ceramic glass foam. Also, in their study, the base glass foam (waste glass) has reported that contains 30% porosity, but these porosities have not the ways to penetrating, and therefore, on the surface of the samples, a layer of glass is densified, which makes the material glazed. In another study, which is made by the SiC waste and glass he achieved a relative density of 0.08 g/cm^3 and 92 percent porosity by adding 12.5 percent of SiC. By SiC addition to the glass, the incidence of the small

and large porosity caused to low surface energy. Brusatin, and colleagues [6] used SiC -β foaming agents and burnt oil ash and soda lime glass at temperatures ranging from 800-900ºC. Mangutova et al. [7] Have been researching several types of waste materials such as metallurgical slag, coal dust and 30 wt.% glass waste with the organic template method for forming the porous structure and glass- ceramics foam. They concluded that by adding 20 wt. % of TV glass waste to the slag the flexural strength would increase from 51 MPa to 75 MPa. This research was carried out to reduce the cost of ended glass and glass ceramic foam, as well as the use of amorphous slag (Slag of Mobarakeh of Isfahan) and window glass waste to prevent the environmental contamination. First, feasibility studies were carried out by preparing different samples of slag without soda lime in several different temperatures. Then, the effect of SiC foaming on physical properties was studied by glass beside the SiC foaming agent at different temperatures and weight percentages of glass and slag. The microstructure, expansion and bending strength were evaluated as well.

2. Materials and Methods

Two batches of glass and steel slag were ground and were fined to a mesh below 150. The presented composition in tables 1 and 2 are related to the XRF analysis of slag and glass compositions respectively. The samples were prepared in tablet form with a radius of 2 cm and a thickness of 3-4 mm using a single-axial hydraulic press, with pressures varying from 50 to 100 MPa. 2 wt.% extra carboxymethyl cellulose (CMC) of raw materials was used to increase adhesion between the particles.

Table 1. The chemical composition of EAF slag

SiO_2	CaO	Al_2O_3	P_2O_5	Fe_2O_3	MgO	K_2O	Na_2O	MnO	TiO_2	S
43.90	37.16	7.18	3.10	1.02	1.17	0.53	0.42	0.39	0.11	0.72

Table 2 The chemical composition of soda lime glass

SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	Fe_2O_3	TiO_2
73	14	9	4	0.15	0.03	0.1	0.02

The letter S , G, denoted for the slag, the glass,. The combination of SG50-5SiC means the base compound (slag 50 wt. % -glass 50 wt. %) plus 5 wt. % of SiC foaming agent. The combination of SG10-5SiC means a composition consisting of 10% glass added to 90% slag, which is added to this total 5 wt. % of SiC foaming agent. Then they entered directly to the tunnel furnace to a temperature of 1200ºC once

was removed after 1 minute. The density of the composition, was measured using the gas picnometry sampler according to (ASTM-D5550). The test was repeated 10 times for each sample and the average was confirmed. Bulk densities of the sintered samples were deter-mined by the Archimedes method AS TM C373 with the below formulation:

$$V = W_W - S, P_t = W_w - D/V, B = D/V \qquad (1)$$

where Ww is the wet weight of sample, S is the immerse weight of sample, Pt is the apparent porosity, D is the dry weight of sample, and V is the volume of sample. The open porosity Po is determined by using the saturated weight Ws,

$$P_O = W_s - D / W_s - S \qquad (2)$$

Scanning electron microscopy (SEM: model JEOL JXA-840) was used in order to observe the microstructure and EDX (Energy Dispersive X-Ray Analysis). Samples were mounted onto the sample holder, coated with gold, and then studied with SEM. Crystalline phase identification was performed on powder made from ground sintered pellets, using X-ray diffraction (Philips Power Diffractometer 1710) with Ni- filtered Cu- K α radiation and the relevant JCPDS cards (Joint Committee on Powder Diffraction, 1972). X-ray fluorescence spectrometer (XRF) (Thermo Scientific Niton XL2) was used to determine major and trace elements in samples.Home made hot stage microscopy (HSM)which can be heated up to 1050ºC using the thermal sensitive camera was used to take the soften images of composites.

To determine the pores size and distribution within each specimen, image analysis of the microscopic images was conducted using SPIPversion 6.7.7 software (Image Metrology 2018). For each specimen, three images at different magnifications (i.e., 20×, 50×,100×, and 200×) were selected. Using images at different magnifications minimized the measurement error

The sample's size for bending strength measuring was 70 × 10 × 10 mm. Five samples were used to each measurement. The flexural strength of specimens was determined by three-point bending test on specimens at a span of 50 mm and crosshead speed of 0.6 mm/ min. DSC analysis (Nietzsche 320, Germany) was utilized to determine the Cp values of composite powder. It was performed using 6 mg of glass powders in an alumina crucible in air at a heating rate of 10°C/min

3. Results and Discussion

HSM images presents the three primary blends of pure slag (S), pure glass (G) and slag-glass mixture with 50 wt. % (SG50) in the temperature from 500 to 1050 ° C to better recognize the softening temperature.

In the case of slag in Fig. 1, it can be seen that the shape and dimensions of slag specimens did not change when the temperature is between 500 and 1000℃ Corresponding to the rigid behaviour of amorphous slag.

However, as expected the soda lime glass (Fig. 2), is softening at about 750 ° C, begins to shrinkage in size and begins to melt at 950ºC.
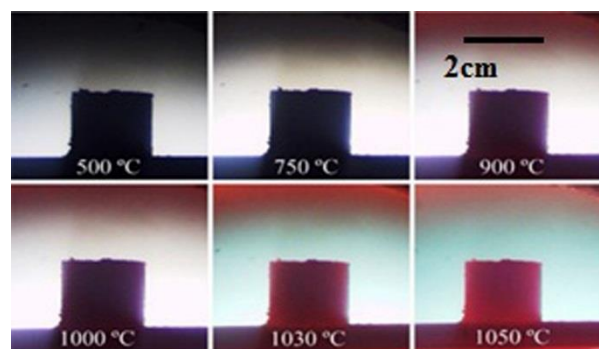

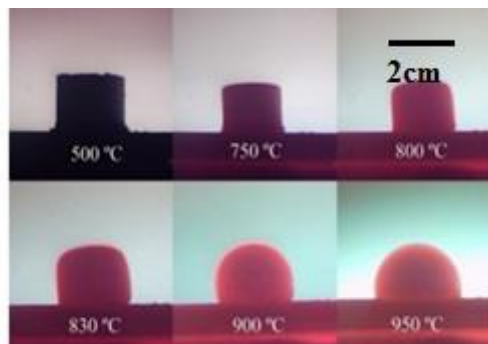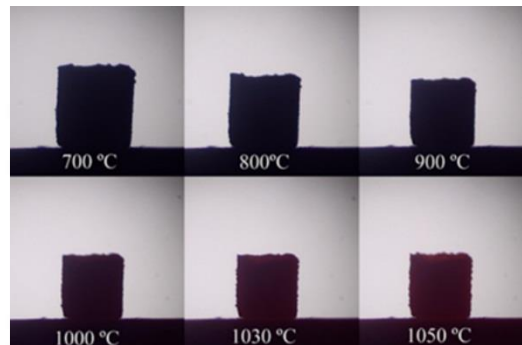**Fig. 1.** Hot stage microscopy images of pure slag

Fig. 2. Hot stage microscopy images of pure glass

It can be said at higher temperature than 950ºC the melted glass could wet the slag particles. In the case of the SG50 mixture (Fig.3), at 800 ° C temperature, the sample's shape was changed due to the glass viscous flow, then the glass phase, moves between the slag particles, as well as filling the empty spaces between the particles and almost 10% (from the area contraction) of shrinkage could be seen


Fig. 3. Hot stage microscopy images of 50 wt. % glass-50 wt. % slag (SG50)

However, the overall shape of the sample is maintained: due to the presence of slag particles with a much higher melting point. Ponsot and E. Bernardo found that a liquid phase of the softened glass can dissolve the inorganic waste of the amorphous slag [8]. From the image of the slag compound at 1050° C, it can be concluded that to the slag dissolving in molten glass phase caused to the glassy wall's formation, the treatment temperatures should be above 1050ºC. For microstructure evaluation, pure slags were sintered at 1180 ºC, 1200 ºC, and 1260ºC, and the SEM micrographs were obtained .

1. 3 SEM Micrographs of Sintered Pure Slag Sample with SiC at Different Temperatures:
SEM images of slag samples sintered at 1100, 1180, 1200, and 1260º C are shown in Figs. 4 .
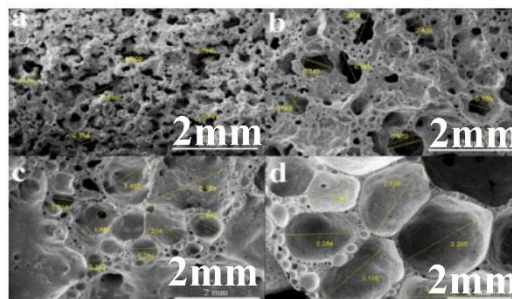
Fig. 4. SEM micrographs of pure slag-5 wt. % SiC sintered at (a)1100 ºC (b)1180 ºC (c) 1200 ºC (d) 1260ºC

At 1100°C (Fig. 4a), the cavity and the cell are not formed. In the process of SiC decomposition, the gas (CO_2 or CO) is generated in the presence of oxygen. The distance remains between the particles by gases production, the tunnel like porosity remain behind gases, as a result, the shape of the foam structure is more similar to the scaffold, because the uniform wall of the expanded porosity is not formed. The average size of the porosity, calculated from the SEM images, is about 500 μm. While at 1180 ºC, the viscosity of slag decreases, the integration of the composition and the adjoining of the adjacent particles occurs, as several cells or bubbles observed in the structure. The average diameter of these porosity increases from 500 μm to 750 μm over the 1100 ºC, but this process seems to have not yet been completed. By increasing the temperature to 1200ºC, pores occupied the most of the volume of the specimenssity of specimens (Fig.5).
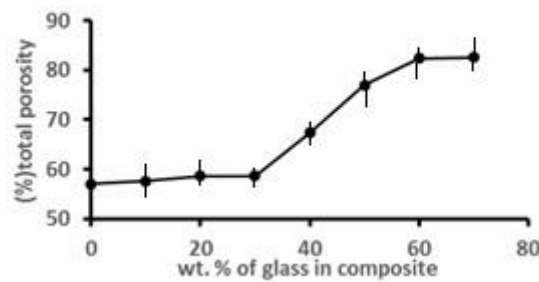
Fig. 5. The total porosity of composite vs. glass wt. % sintered at 1200°C

The average diameter of these porosity is up to 1000 μm. This continuation of the temperature up to 1260°C only increases the porosity and thinness the walls. The average diameter rises to about 3 times, 2800 μm.

2. 3. Specification of the Physical Properties of Glass – Slag-SiC Composite with Glass Amounts

The waste glass was added to the mentioned slag composition to improve the sintering ability and softening properties, while maintaining the advantage of using waste and cheap materials. To measure the optimal amount of glass waste, eight different glass weight with 0 to 70 wt. %, as listed in table 3, were added to the slag.

All samples were mixed with the 5 wt. % SiC, to evaluate the sufficient foam availability. The variation of the density values by the glass's amounts added to the slag presents in Fig. 6.

Table 3 The wt. % of added glass to each composite

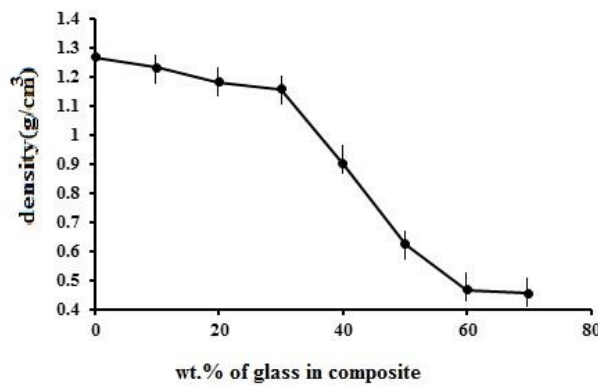| sample	SG0	SG10	SG20	SG30	SG40	SG50	SG60
Wt. % of added glass	0	10	20	30	40	50	60

Fig. 6. The density of glass-slag composites vs. glass wt. % sintered at 1200°C

In general, the curve in Fig. 5 shows the density loss by the more glass addition. Apparently by the glass content up to 30 wt. % the viscosity's decreasing was happened. From this point, it can be said that there was a sufficient glass melt phase to form the bubble's wall [9]. But, by adding 40 wt. % of glass, the first density depression step occurs, the density in SG30 (1.15 g/cm^3) decreased to 0.89 g/cm^3, in SG40. This trend continues from the SG50 to SG60 sample with a lower slope. The reason of the density's decreasing is the coherency among the porosity (low surface tension of melt and the growth of porosity occurred) [10] this phenomena increases the porosity' size, which result in a severe strength's reduction [11]. The process of porosity coherency continues to SG70, and in fact, the process of the volume expansion (reduced density) stopped. The total porosity, vs. glass wt. %, is presented in Fig. 6 .

According to the foam definition, the total porosity should be higher than 20-30 wt. %. The open and closed porosities of samples are also shown in Fig. 7.
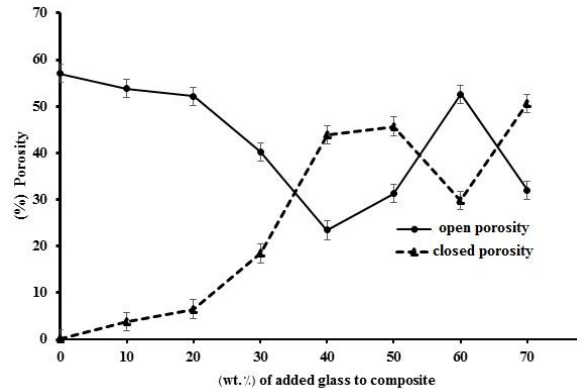
Fig. 7. The open and close porosities of glass- slag composite vs. glass wt. % sintered at 1200ºC.

Closed porosity increases with a sharp slope up to 40 wt. %. glass. This trend continues with a slighter slope up to SG50 with the 45% closed porosity. The viscous phase , the gas-containing bubbles and the closure of surface porosity by viscous phase, are the main reasons for the closed porosity formation. However, the vital point of this curve is the closed porosity reducing from the case SG50 to SG60 and it increase in the case of SG70. Generaly, by glass addition, the total viscosity and the surface tension of the entire sample reduced , the gas destructed the wall of the bubbles, causes the porosity to reach each other and to the surface [12]. Therefore, the open porosity increases while the closed porosity decreases [13]. Once again, with the excessive loss of viscosity and the surface tension in the melted glass, in the case of SG70, the capillary forces between the particles, easily created the melt at the surface and the walls of closes porosity. On the other hand, the pressure of the gas, while joining the porosity to each other, merges the walls [14], and repairs the surfaces [15]. Fig. 8 shows the microstructure of a glass-slag composite with the different wt. % of glass at 1200 ° C.
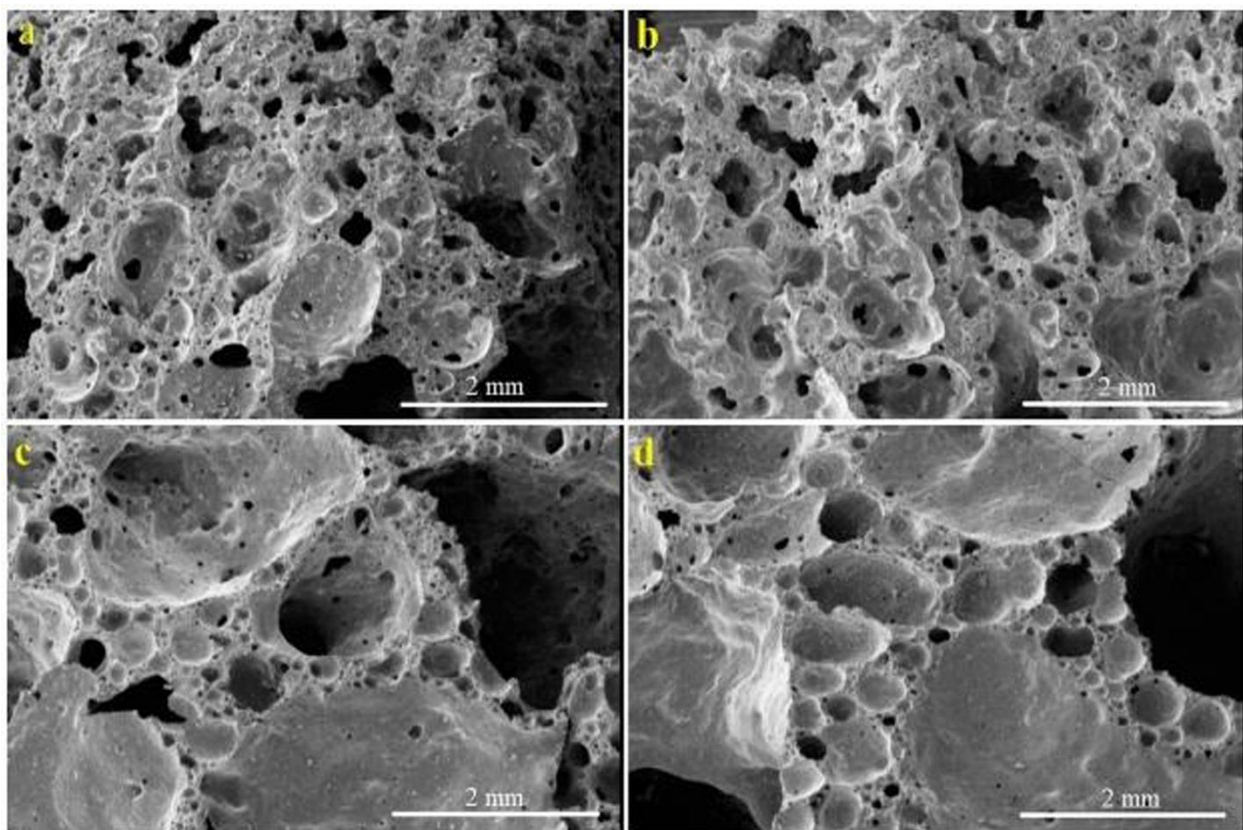
Fig. 8. The microstructure of a glass-slag composite with the different wt. % of glass sintered at 1200 ° C.(a) 30 wt. % (b) 40 wt. % (c) 50 wt. % (d) 60 wt. %

In the case of SG30, non-spherical holes with jagged edges, appear due to the lack of the sufficiently melted phase [16]. Apparently, the glass, has not been added sufficiently to dissolve the slag particles , to create a melt coating on them [17], and the sharpness of the unsolved particles is visible at the edges of the porosity. This process, has been improved in SG40, and a limited number of spherical porosity, have been formed. However, for the same reason, as in the earlier (Fig. 4), the spherical porosity has no uniform and closed walls, and most of the porosity, are deep and tubular. By increasing the glass content to 50 wt. % in Fig. 8C, most of the pores are spherical , also they are more uniform. In Fig. 8d, (in the case of SG60), the growth of porosity, the smoothness of all surfaces and the sharpening of the walls between the porosity have been occurred. The average (about 10 numbers of pores in one line) pores size of the SG30, SG60, SG50 are about 190 μm , 150 μm ,130 μm respectively. (SG70 was not shown). The size reducing of the porosity has coincided with their amount's increasing (Fig.6). An important part of this reduction is due to the enormous quantities of porosity below 50 μm in SG40.(first the glass content decrease the pores size, because of pores filling, then by increasing the glass content the slag solvation occurs probably the surface tension decreases which led to the gas expansion and porosity growth .

However, this sliding trend does not continue in the case of SG50. In SG60 (Fig. 8d), the average size of porosity is about 270 μm. With the growth of the porosity, the distribution of cavity size in this sample (SG60) has increased significantly. For the above reasons, the SG50 was chosen as the most suitable base composition for the studying of foaming agent.

3.3. Examination of Different Sintering Temperatures for the SG50 - SiC
The combination of SG50 and 5 wt. % SiC foaming agent was mixed, different sintering temperatures from 850ºC to 1290ºC were performed. Fig. 9 shows the image of the samples after sintering. The volume of the specimens increased with the sintering temperature.

At the temperatures of 1290 ° C, due to the expansion, the deformation of samples was occurred and became like glass shells (Fig. 10).
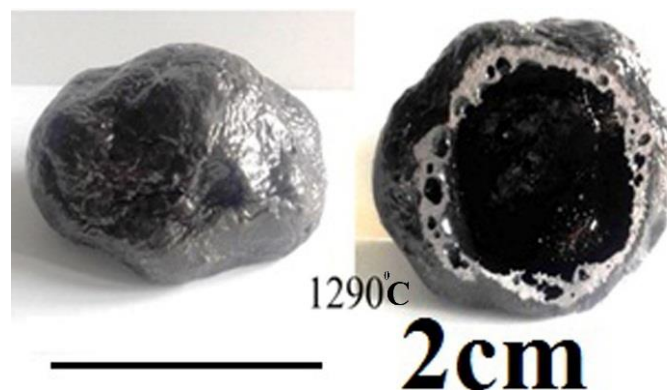

Fig. 9. The appearance of surface and under layer of SG50-5SiC at 1290º C

Fig. 10. The appearance of SG50-5SiC sintered at different temperatures.
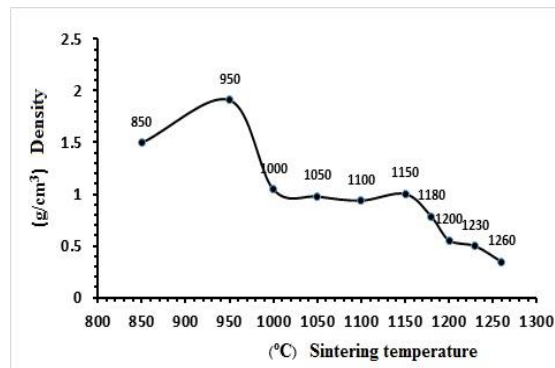
Fig. 11. The total porosity of SG50-5SiC vs. sintering temperature

Therefore, they were not capable to examination in terms of density and dimensions, and were discarded. Fig. 11 shows the density vs. temperature up to 1260 ° C in SG50-5SiC.

The density decreases with temperature in Fig.9. Whereas, the density has significantly increased from 1.5 to 1.9 g/cm^3 at 850° C to 950ºC temperature range. This can be related to the viscous flow of the glass phase which fills the spaces between the particles. Probably, the total viscosity of the composite has not been low enough to withstand the exhausted gases. Therefore, sintering shrinkage can easily overcome the gas pressure of the foam reaction [18]

At 950°C, by decreasing the glass's melt viscosity, the sample withstand exhaust the volume of sample increased. (the low viscous glass can move and the produced gasses could spread under the melt , but viscous glass could not move and the trapped gas destroyed the melt surface). From 1000º to 1150ºC, since the slag is still not sufficiently soft, so it does not play a role in the foaming and forming of bubbles and it is still the melt of the glass that increases the volume of sample. However, at higher temperatures than 1150ºC, slag seems to have an effect on foaming, and the density has increased with a steeper slope. The decrease in density with further temperature continues because the pressure of the exhaust gases overcomes the molten surface tensile and causes more expansion [19-21]. In Fig. 12, the porosity vs. the sintering temperature has been presented.
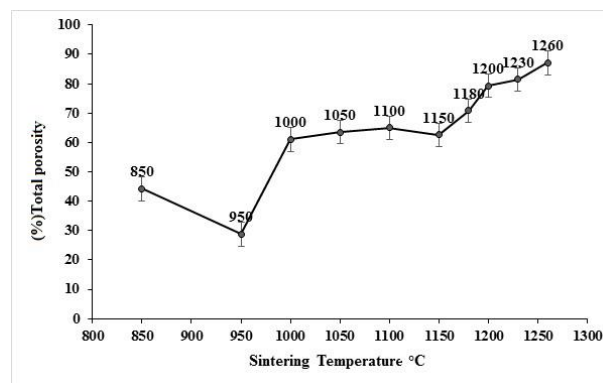

Fig. 12. The total porosity of SG50-5SiC vs. sintering temperature

It should be noted that, according to the specifications given in the sources [20-23], the relative density of foam should usually be less than 20 to 30%. Based on this definition, the first point (total porosity fraction of 100) becomes up to the 30% occurs at 1180ºC, which reaches to 29.17% relative density. The longitudinal expansion presented in Fig. 13.
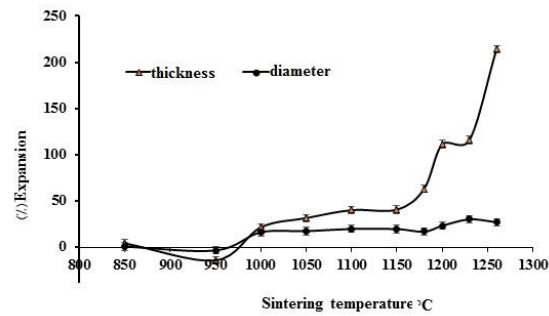
Fig. 13. The longitude and axial expansion of composite by sintering temperature

The 14% contraction at 950 ° C, then a roughly constant expansion at 1150 ° C, the increase in the longitudinal expansion slope from 1150° C to 1200º C, corresponding to the increase in density. The expansion development from 1200°C to 1230° C does not change much (111 to 115%), but from 1230°C to 1260º C, with the viscosity reduction, gas pressure easily expands the bubbles too much. and they connect them together, as a result, the expansion rises from 214% to 328%. Continuing this process to 1290 ºC, all gases accumulate in one or more limited bubbles and with the pressure on the thin-walled specimen, the bubble (or porosity) like the dome-

shaped, as shown in Fig. 9, will eventually remain. Expansion of foam specimens, especially by fast heating, is further enhanced by thickening. The reason of thickness expanding is related to the exhaust gases' tendency to move towards the surface, due to the downward pressure of the molten masses [23-28]

4.3. Phase Evaluation
Fig. 14 shows the X-ray diffraction pattern of four composites with different glass contents sintered at 1200ºC.
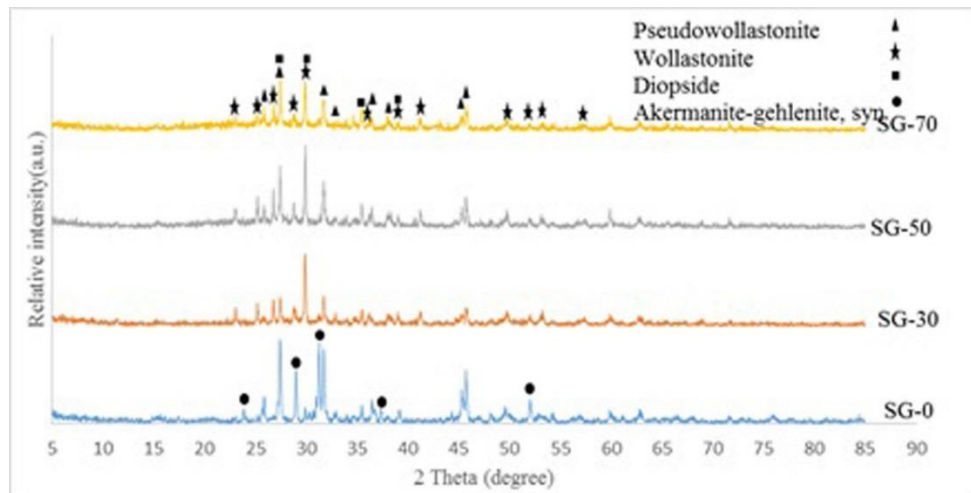
Fig. 14. X-ray diffraction pattern of four composites with different glass contents sintered at 1200°C.

In the SG0 sample, the akermanite-gehelnite and diposide phases are crystallized with the wollastonite phase. By increasing the amount of glass, this phase is replaced by pesodo-wollastonite. In fact, the elements contained in akermanite-gehelnitis are involved in the structure of calcium silicate and wollastonite. The transformation of wollastonite to pseudo-wollastonite at 1125 ° C has been reported at low pressures by geologists. The pseudo-wollastonite phase is a ring silicate with in-congruent melting and a wollastonite is chain silicate with a congruent melting [22] that can be explain the uncontrollable expansion of the samples at high temperatures.

These composites suposed to be used as paving materials. The bending strengths of obtained porous composites were measured and were reported in Table 3. Construction foam materials have usually compressive strength of at least 0.8 – 1 .0 MPa; however it is though t that by comparing to the other porous products, these samples have reasonable strength in 2-5 MPa , although the porosities were not adequate, but the porosities binding was strong enough to have light and strong samples. The Cp values of samples also were reported in Table 3 , which have been used the powder form of composite .

Table 3 The Bending Strength and C_p values of composites

SG70	SG50	SG30	Sample
3.2	4.8	2.5	Bending strength (Mpa)
0.28	0.34	0.38	$C_{p(j/k.mole)}$

Conclusion

By increasing the glass contents up to 50 wt.% to the steel slag composite, the foam ability was improved, because of the decreased viscosity and surface tension of the resulted composite

The optimum foam temperature for the slag composite with 50 wt.% glass was 1200 ° C by 20ºC/min and 3 minutes holding time.

By adding the glass to the slag up to 30 wt.%, no change in the residual porosity is observed, but by adding this weight to over 30 wt. %, the total porosity increase significantly to 80%.

With the glass phase, the shape of the porosity changes from the tunnel to the spherical.

The dominant phase wollastonite and pseudo-wollastonite crystallized from a slag composite with 50 wt.% glass at temperatures above 1100 ° C.

Acknowledgements

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