



Compressibility and Foaming behavior of steel slag/waste glass composites by particle size distribution and foam agents

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ABSTRACT

In present research, the foam glass-ceramic composites fabricated by window glass, steel slag and SiC, CaCO₃ foaming agents were investigated by press-sintering method. The optimum sintering temperature was obtained at 1200°C with a 3-minutes holding time and 20°C/min heating rate. The optimum pressure level of 80 MPa for achieving the 70 % of relative density was selected. The effect of particle size distribution of starting materials on the green and fired density of resulted glass-ceramics composites was evaluated. The composite's green density was 1.7g/cm³ obtained using the following particle size (49 wt. % 150µm, 21wt. % 85µm, 21wt. % 65µm, 9wt. % 45µm). It was shown that using medium-fine grade of the slag powder, the compaction and green densities of samples were increased up to 16% while in the case of slag/glass composites (due to the high hardness of the glass powder), the compaction of composite was increased 11% compared to the coarse grade particles bearing samples. It was observed that finer particle sizes (below 75 µm) significantly cause more foaming and lower density (about 80 wt. % porosity). This can be due to the faster coalescence process and gases trapping which was arisen from the decomposition of foam agent.

1. INTRODUCTION

The most numerous types of waste are slag ones produced by various industries. The largest producers of slags are metallurgical manufacturing and thermal power plants (TPP) that produce heat by coal-burning [1]. The forecast for the development prospect is to produce 55 million tons of steel in Iran, which 20% of it is in the form of the slag. Namely, in 2025, 10 million tons of the slag will be produced in the country. Slag is now being used in various industries such as cement, roads, buildings, and agriculture, but high volumes of this valuable material are still being accumulated. Foam glass (FG) is a porous glass material composed of waste glass and various mineral waste materials. Generally, the production process of the foam glass is as follows: Firstly, a uniform mixture is formed by adding appropriate amounts of the foaming agent, solvent, and various modified additives. Then, the uniform mixture is put into a specific mould and subjected to preheating, melting, foaming, cooling, and other processes [2].

Another method is the simplest technique based on powder sintering with the incorporation of foaming agents. This method was employed in the present investigation. Incorporation of foaming agents is generated porosity by emitting gas during the reaction at elevated temperatures [2-4]. During sintering, the foaming may be caused by an oxidant ion effect, which is typical for C-based "foaming agents", namely C (graphite, carbon black, coal, etc.) and SiC or by a decomposition process of minerals like carbonates (Na₂CO₃, CaCO₃, MgCO₃, etc.) or sulfates (CaSO₄, i.e. gypsum) [5-9]. They found that SiC reinforcement in aluminum alloys improves the strength of the foam. The studies have found that the foam undergoes a deformation layer. The efficiency of impact absorption is increased because of such deformation behavior. Studies mention that energy absorption of any foamed material is a function of its plateau stress. The iron foam producing by foaming, which has high porosity and can be low-cost mass production, is difficult. The reasons are related to the high melting point, high density, high

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surface tension, and low viscosity of the iron slag. Analysis of compaction diagrams leads to the conclusion that various factors play an important role in the compaction process. The size and the shape of each particle should be specially pointed out [10]. It was shown that foam glasses with a density of $<150 \text{ kg.m}^{-3}$ are obtained when the particle size is $\leq 33 \mu\text{m}$ (D50). The resulted foams of this work had a homogeneous pore distribution and major fractions of them are smaller than 0.5mm. Simply by smallest particles ($13 \mu\text{m}$), the pore size is increased to 1-3mm due to a faster coalescence process [11].

The present paper aims are to reuse steel slag in the production of glass-ceramic foams. In the present study, calcium carbonate (CaCO_3), SiC, window glass were used to produce glass-ceramic foams. The size and morphology of particles, the pressing conditions, the green, and sintered densities, the sintering temperature was systematically studied. During the heating process, the carbonate ions decomposed to generate CO_2 gas so that the softened glass phase forms and the gas is then enclosed by the glassy phase, producing a porous structure in the sintered samples at the end [7-10]. Relationship between glass addition and resultant

porosities and the densities of produced foams from selected mixtures of slag and glass were studied.

2. MATERIALS & METHODS

In this work, the steel slag of electric arc furnace (EAF) of Mobarake Company with the chemical composition in Table 1 was used.

TABLE 1. Chemical composition of steel slag (wt. %)

composition	wt. %
SiO_2	43.9
CaO	37.8
Al_2O_3	6.72
P_2O_5	3.7
Fe_2O_3	1.8
MgO	0.95
$\text{K}_2\text{O}+\text{BaO}$	4.53
Na_2O	0.3
MnO	0.2
TiO_2	0.1

The XRD pattern confirms the amorphous structure of the slag in Fig. 1.

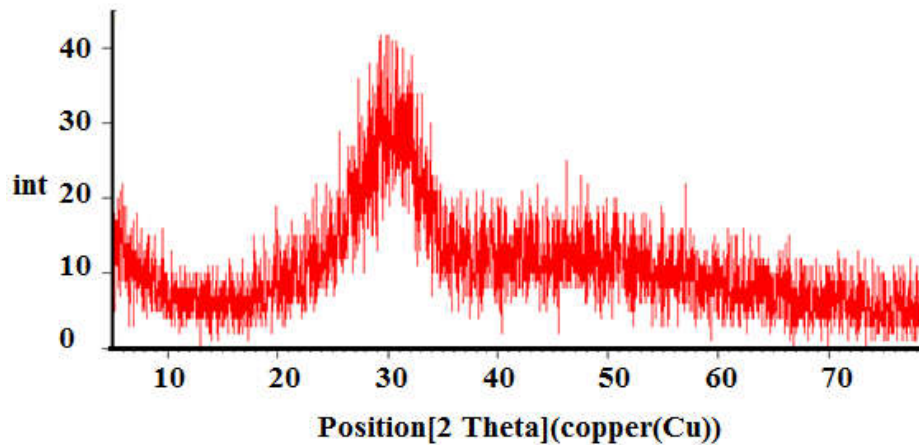


Figure 1. The XRD pattern of steel slag

XRD measurements were performed using a Scintag X1 advanced diffraction system with the $K\alpha$ Radiation ($\lambda=0.154\text{nm}$). The thermal expansions measurements were conducted in a dilatometer (model Nietzsche-E402, Germany) using a silica probe.

DTA analysis (Nietzsche 320, Germany) was utilized to determine the crystallization temperature of the glass. It was performed using 6mg of glass powders in an alumina crucible in the air at a heating rate of $10^\circ\text{C}/\text{min}$. DTA and dilatometer results of the fine pure slag and slag/glass composite were represented in Figs. 2 and 3.

It can be seen from Figs.2a and b that the softening points of sole slag sample and slag/glass composites have not effective differences and they are around 601°C , but the softening range by the glass was wider than the pure slag sample. In addition, a very trace exothermic temperature around 950°C can be seen in DTA result of slag/glass blended composition (SG50)(see Fig. 3). The slag powder was melted in an alumina crucible in 1450°C and then water quenched to achieve a homogenous amorphous glass. The Electric crusher was used for grinding of window glass powder and then was milled in a conventional ball mill for 2 hours to make it finer. Slag and glass powders were

classified in particle sizes by sieving in vibrator sieve shaker. 12 Batches were selected from five different particle size range: A: 180-250 μm , B: 150-180 μm , C: 75-150 μm , D: 45-75 μm , E: <45 μm and AG, BG, CG, DG, and EG are equal to those powders in the slag. Table 2 corresponds to wt. % of different particles which were sieved and blended accordingly. The first six samples were selected from the pure slag and the rest of them were slag-glass mixed with 50-50 wt. % ratio. Codes of S1-S6 and GS1- GS6 corresponds to pure slag mixtures and slag-glass, respectively, with completely similar particle size distribution.

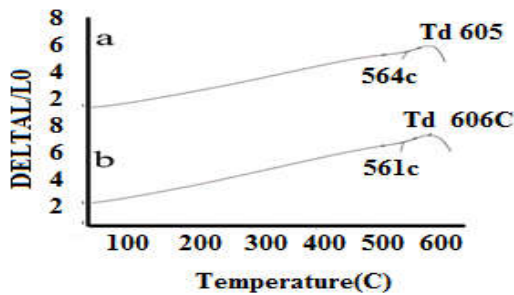


Figure 2. Dilatometer results of (a) pure slag (b) slag-glass composite powder.(the softening temperature)

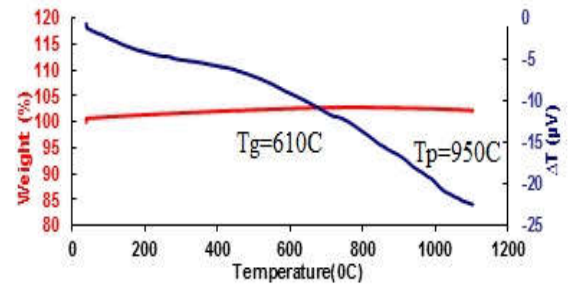


Figure 3. DTG results of slag/glass(SG50) powder

Foam agents used in this study were CaCO_3 and SiC , all with industrial purity. A tubular mixer for 20 minutes mixing of each sample batch was used. The mixed slag/slag glass powder with or without foaming agents was uniaxially compressed into pellets with 20mm diameter and 4mm thickness. The applied pressure was in the range of 50 to 100 MPa. Compressed powder compacts were sintered in an electric heating furnace under atmospheric conditions. Sintering was done at 1200°C in 3 min with a heating rate of approximately $20^\circ\text{C}/\text{min}$. Bulk density, apparent porosity, water absorption, and volume change of sintered specimens were characterized according to the procedure described in ASTM-C20 methods.

TABLE 2. The particle size distribution of different composites

NAME	Sample S1				
	A	B	C	D	E
Mesh number	60-80	80-100	100-200	200-325	-325
Particle size (μm)	250>X>180 wt.%	180>X>150 wt.%	150>X>75 wt.%	75>X> 45 wt.%	X<45 wt.%
S1	-	25	25	25	25
S2	-	21	49	9	21
S3	-	49	21	21	9
S4	-	9	21	21	49
S5	-	-	10	30	60
S6	15	30	40	15	-
GS1	-	25	25	25	25
GS2	-	21	49	9	21
GS3	-	49	21	21	9
GS4	-	9	21	21	49
GS5	-	-	10	30	60
GS6	15	30	40	15	-

3. RESULTS & DISCUSSION

The composites were selected with four different particle sizes established upon Table 2. contains the four altered powder sizes (B, C, D, E), which their wt. % were equal (25%).

samples S2 and S3 consisted of 70% coarse powder (B+C=70%) and 30% fine (D+E=30%). The average particle size in sample S2 is smaller than sample S3 because it has more amount of C and E. In the case of sample S4, in contrast to samples S2 and S3, a finer mixture containing 70% fine (D+E=70%) and 30%

coarse (B+C=30%) were used. Sample S5 was also a very fine mix (E=60%, D=30%, C=10), and the sample S6 was very coarse (A+B=90%).

According to Andresen equation [4], for high compaction, we have corresponded to the percentage of the volume of particles smaller than the desired size.

$$CPFT = \left(\frac{d}{D}\right)^q \times 100 \tag{1}$$

If we consider $d_{min}=85\mu m$ and $D_{max}=150\mu m$, $q= 0.5$ to 0.33 . It can be concluded that the volume percentage of particles finer than $85\mu m$ should be changed between 77% and 82%. These particles volume % conditions were involved in the case of samples S2 and S3 which could explain the better compressibility of the mentioned samples (see Fig.4). The green density versus pressing pressure of the fair slag bearing samples and the slag-glass composites were presented in Figs. 4 and 5 respectively.

It can be expressed that by increasing the pressure up to 70MPa, the samples are not more compacted and green densities of samples are not increased. In the case of the

sample S5, due to the existence of more fine powder size, the plasticity of powders is increased, also, the wide particle size distribution of this sample is caused to the more compaction and the alteration of pressure vs. density is turned in to linear, as shown in Fig.4.

The compaction behavior of samples S4 and S5 showed that if the distribution of finer particles and the smallest volume of powder are overcome, the compressibility will be improved. The samples S2 and S3, which have 70% coarse (B+C=70%) and 30%, fine (D+E=30%) particles, showed the similar compaction but comparing to S4 (the higher coarse amount of sample S4), they were compacted 10% more. Obviously, the fining of the powder (S4) do not necessarily result in improved raw density, but the distribution of the fine grain powder can lead to more compaction(44%) in the case of S5 [10-12]. By comparing density results of Figs. 4 and 5, it can be seen that the density and compressibility of composites are 13% less than pure slag samples. This can be attributed to the lack of plasticity in glass particles or the higher hardness of glass particles [13].

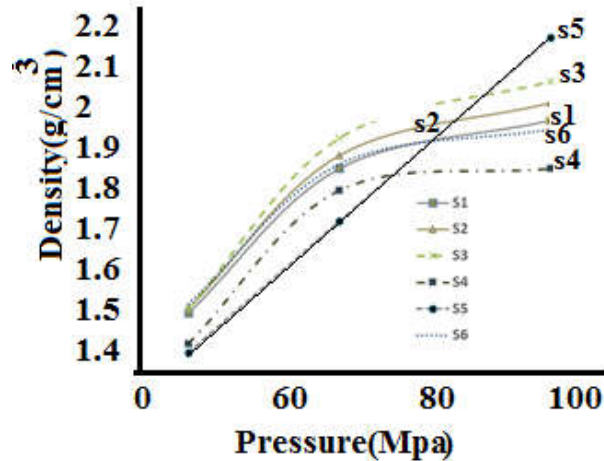


Figure 4. The green densities of lone pressed slag samples with different particle size distribution based on Table 2

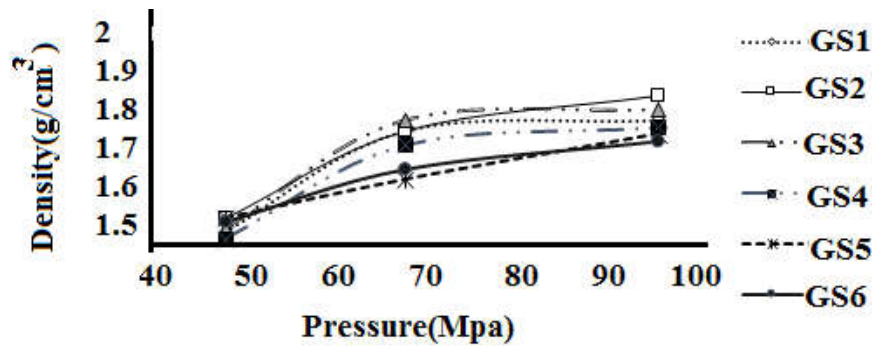


Figure 5. The green densities of slag/glass composites with different particle size distribution based on Table 2

In the case of pure slag samples (Fig. 4), it is observed that by increasing the pressure up to 70 MPa, the density-pressure slope is initially high, and after the maximum value of green density, this trend is decreased. The smaller particle size of sample S5 and the broad distribution of fine particle size caused to the best compression behavior (2.2g/cm^3). In addition, adding the glass to the slag composition decreased the green density up to 12% (GS5). It is well known that the densities of the slag powder. Glass and the mixed

powder are 2.95 g/cm^3 , 2.52 g/cm^3 , and 2.7 g/cm^3 in that order. Thus, 8% of this trend (a 12% decrease in density) is due to the different glass and slag powder density. However, 4% of this trend has another reason, which seems to be due to the lower compressibility of the GS5 comparing to the S5, i.e. higher friction and rigidity of the soda lime particle in contrast to the slag can be led to the low compressibility. SEM images of slag and glass particles (see Fig. 6) confirm this statement.

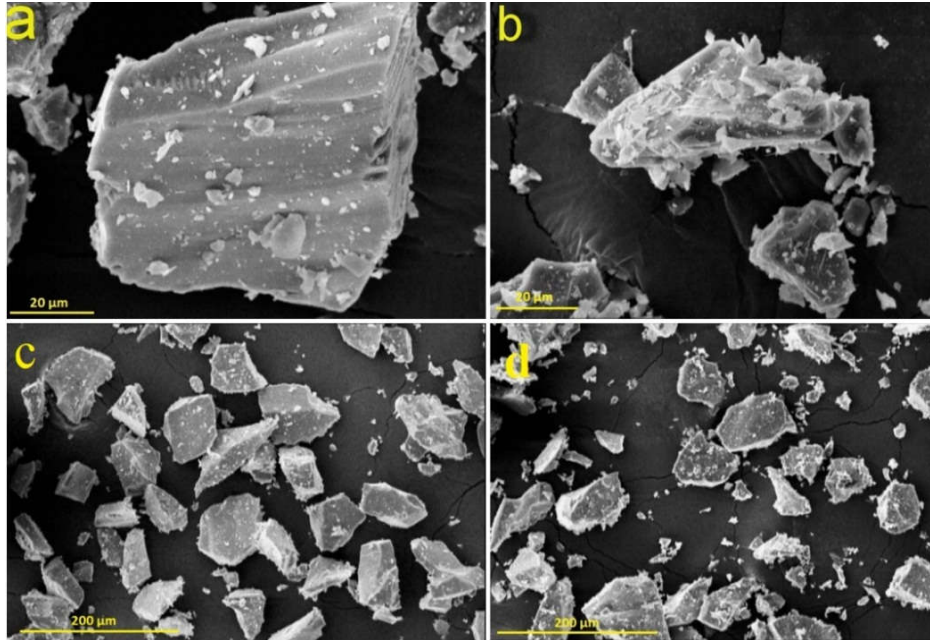


Figure 6. SEM images of glass and slag particles

Although there is no very significant difference between shapes of particles in the case of slag and glass powders, the jaggy surface of glass particles, which is created during the grinding process, can increase the friction between particles causing a decrease in the compressibility of the mixed powder. By fining glass particles, the rougher surface is created. They can resist compression and reduce the green density.

Flowingly, to evaluate the foaming ability, the GS2, and GS3, which have a high green density and wide particle size distribution, and GS4 and GS5 with a lower green density were blended with the foaming agents of SiC and CaCO_3 and were sintered at 1200°C by $20^\circ\text{C}/\text{min}$ heating rate and 3 minutes holding time. Densities resulted from each sample are shown in Table 3.

The sintered densities of samples vs. the average particle size are presented in Fig. 7.

By increasing the average particle size, from the GS5 sample to the GS3 one, the density was increased and the foaming ability was reduced. It is well known that in

glass powder with smaller particles, the surface coagulation phenomenon occurs faster, and the melted particles form the walls to arrange the gas trapping [14]. For this reason, the gas from the foaming agent decomposition cannot be escaped from the hole, and by pressure on the film of glass walls, the volume and porosity is increased [14-16]. Figure 8 shows images of foams developed by 4 different base powders and two foam agents including CaCO_3 and SiC.

TABLE 3. Composition and density of sintered samples

SAMPLE CODE	Base	Foam agent wt.%	Density (g/cm^3)
GS2-SiC	GS2	5% SiC	0.80
GS3-SiC	GS3	5% SiC	0.70
GS4-SiC	GS4	5% SiC	0.53
GS5-SiC	GS5	5% SiC	0.51
GS2- CaCO_3	GS2	5% CaCO_3	0.84
GS3- CaCO_3	GS3	5% CaCO_3	0.80
GS4- CaCO_3	GS4	5% CaCO_3	0.47
GS5- CaCO_3	GS5	5% CaCO_3	0.43

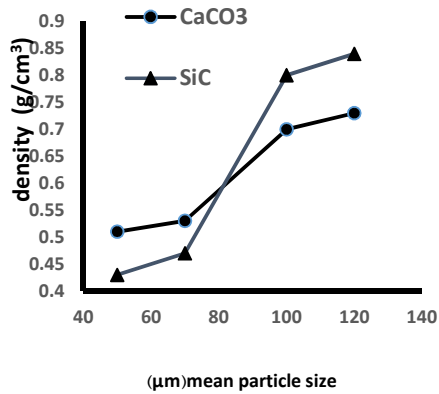


Figure 7. The bulk density vs. average particle size of samples containing two different foaming agent



Figure 8. Images of foam composites developed by 4 different base powders and two foam agents including CaCO₃ and SiC

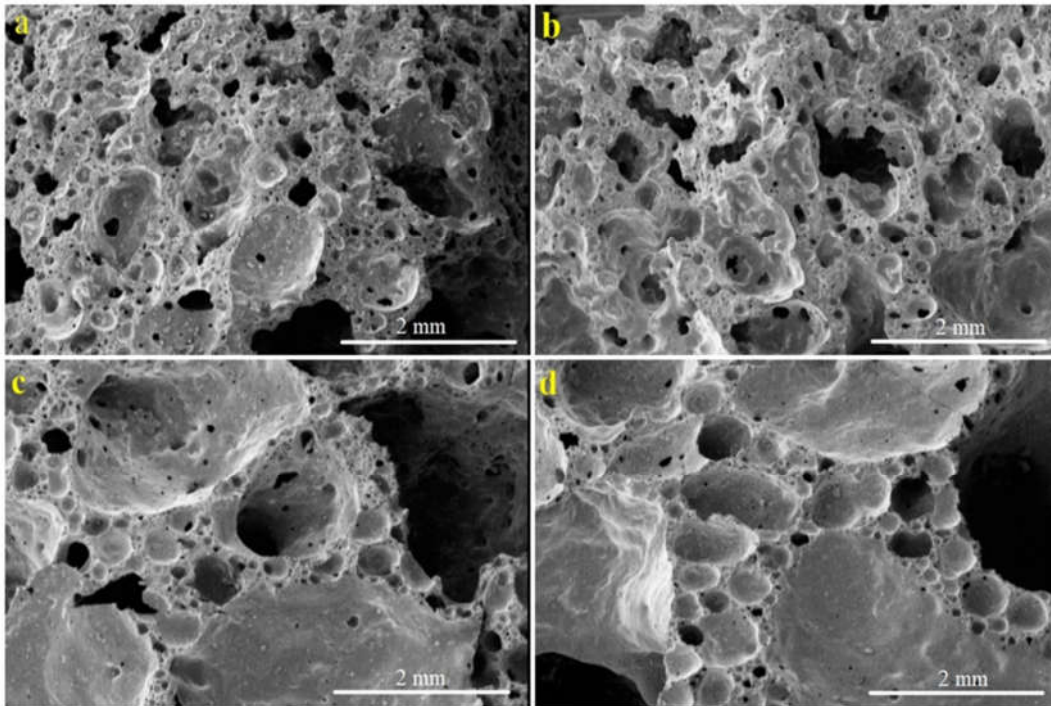


Figure 9. SEM micrograph of (a) GS2 (b) GS3 (c) GS4 (d) GS5

In the GS4 sample, more micron porosities can be seen on the cell wall, but in GS5, the walls are a little smoother and less cavernous. This phenomenon (the lower density of GS5) is due to the quick and easier coalescence of fine-grained composites and the compensation of the gap between particles with the movement of the melted glass. It can be concluded that just high green density does not improve the synthesis and foamability of the composition, but it is the number of fine particles that make walls are uniformly formed and therefore increased in volume [10].

According to the slag thermal analysis, the crystallization temperature was 850°C with 10°C/min heating rate. However, the sintering is at 20 ° C/min heating rate means the heating rate of sintering is very high comparing to the thermal analysis, so, the delay crystallization is reasonable.

The cross-section of CaCO₃ bearing samples is well illustrated in Fig.9. In the case of GS3 and GS2 specimens, due to the coarse size of the particles as well as the fusing and melting of the particle's surface, the uniform wall was not formed to make the gas bubble in

the melt [10,11]. Whereas the GS4 and GS5 specimens were melted faster due to the presence of fine particles and the volume was increased with the formation of the gas.

3.1 Effect of sintering temperature on the microstructures of GS5 composite.

The GS5 sample was sintered at a different temperature to find the appropriate foaming temperature and microstructure evaluation. Figure 10 shows the SEM micrographs of resulted samples.

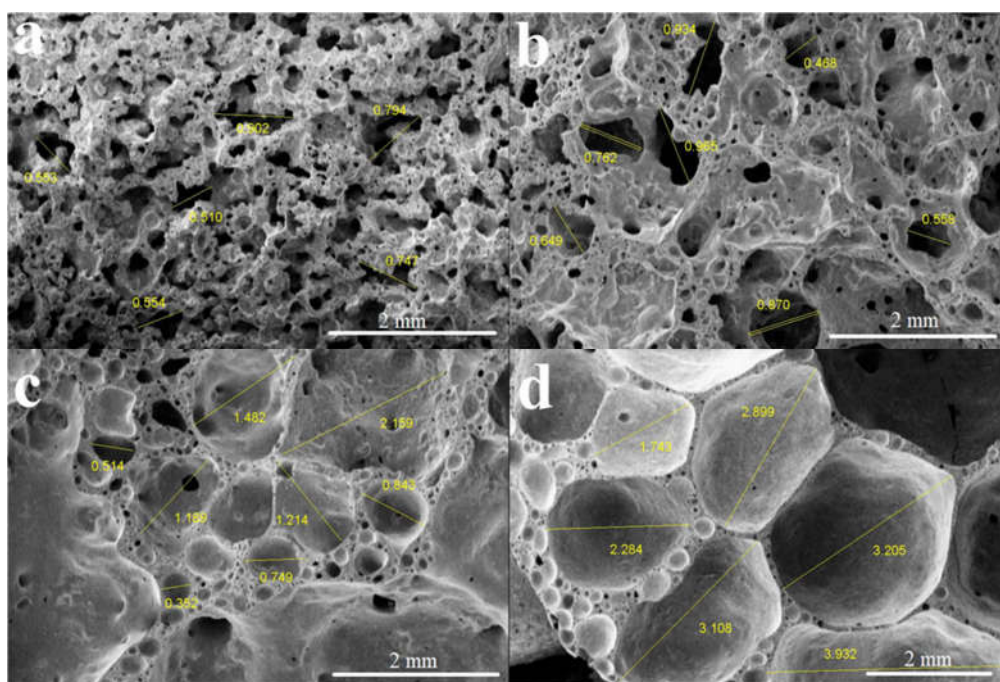


Figure 10. The SEM micrograph of sintered SG5 at (a)1100°C (b) 1180°C (c) 1200°C (d)1260°C

According to Fig.10a, the cell and porosity were not formed in GS5 at 1100°C. However, the formed gases from the foaming agent decomposition exited between the remained gaps of particles (which were not filled with the melted glass) and the tunnel form porous were remained during escaping. The resulted structure owing to the lack of adequate porous expansion is stud like one, therefore, the average mean size of the porosities was calculated 500 μ m. Whereas at 1180°C, by viscous flow, the integration of the composition as well as joining of the adjusted particles occur and some cells can be seen. In relation to Fig.10b, the average size of the porous were raised up to 750 μ m, as the sintering temperature was increased to 1200°C. The volume of samples was filled with the expanded leaving gases and then the average porous size was changed to 1000 μ m. By increasing temperatures up to 1260 ° C, the further increase in temperature just causes the walls to become thin and the growth of porosity happened.

3.2 Phases evaluation

X-ray diffraction (XRD) analysis was performed on four samples in order to investigate the phase changes of the

foaming agent bearing composite by sintering temperatures variations. Figure 11 shows the XRD patterns of the sintered samples at 850, 1100, 1200, 1260°C.

In spite of the DTA peak at 850°C, no crystallization was happened at 850°C due to the high heating rate and short holding time of sintering and two realized phases in patterns belong to SiC and the other relate to the SiO₂. The SiO₂ can be related to the incomplete crystallization of slag and glass compositions at 1100°C. And the crystalline phases are Pseudowollastonite and Wollastonite.

At higher temperatures than 1200°C, the remained wollastonite and pesodowollastonite were increased and finally at 1260°C the only phase was pesodowollastonite. The conversion 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 a chain silicate with a congruent melting [14] that can be explained the uncontrollable expansion of samples at high temperatures.

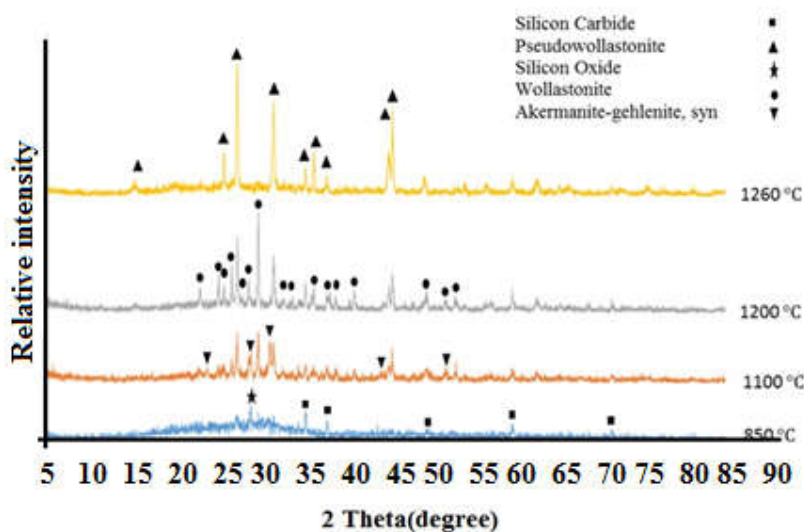


Figure 11. XRD patterns of SG50 using SiC and CaCO₃ foaming agent at different sintering temperatures.

4. CONCLUSION

The 50wt.% soda lime glass and 50wt.% slag composites were pressed and the optimum pressing conditions in the point view of particle size distribution and pressing were systematically studied. It was shown that by widening of the coarse range of the glass powder (larger than 75 μ m), the green densities of samples rise to 11%. The mentioned increase was 16% in the case of samples prepared by slag-glass composites with finer powder (smaller than 75 μ m). These behaviors can be related to the different hardness of the slag and glass powder so that the mismatch hardness led to the weak compressibility of samples. The samples with high green density not only are necessarily appropriate cases for the foaming process, but also the samples with more finer distribution even though with less green density had significantly better foaming behavior and lower density.

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