Properties of foamed glass upon addition of nanocarbon and sintering temperatures

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ABSTRACT
As a blowing agent, 2–10 wt% of nanocarbon (NC) was added 10 µm glass powder (CaO, MgO, Al₂O₃, SO₃, 83 wt%-SiO₂) and sintered at 700–900°C to fabricate foamed glasses with closed pores that were 62–2200 µm. Optical microscopy was used to examine the microstructure and pore size. Compressive strength tester and a heat flow meter were used to examine the changes in mechanical strength and thermal conductivity. The microstructure examination results showed that was performed at 700°C, 297.9–351.3 µm pores were fabricated, and the porosity was 57–63 % in the sample that contained 6–10 wt% NC. At sintering temperatures above 750°C, the pore size increased as the NC content and the sintering temperature increased. The thermal conductivity was maintained at less than 0.28 W/m-K. Therefore, it is possible to use 6–8 wt% NC as a blowing agent in glass material to produce foamed glass that has closed pores of approximately 500 µm with better or equivalent compressive strength and thermal conductivity properties than existing 1000 µm grade foamed glass, despite being sintered at a temperature of approximately 100°C lower.

1. Introduction
Foamed glass is a porous material that has a fine porosity, and it can be used as thermal insulation owing to its excellent corrosion resistance and low thermal conductivity. It also has many industrial applications because it is light-weight and easy to process [1].

The pores in foamed glass can be divided into open pores and closed pores. Foamed glass with open pores is used as sound-absorbing material and general thermal insulation [2]. Moreover, foamed glass with closed pores has excellent corrosion resistance and is light-weight owing to the independently formed closed pores. Because of these properties, it is used as an internal lining material to protect the flue gas desulfurization (FGD) chimneys of thermal power plants. Currently, borosilicate lining blocks with 10 % boron content and 1000-µm grade pores are used as lining materials to protect thermal power plant chimneys. However, there have been reports of problems in which the usage life of the entire system is reduced owing to the abrupt fires occurring the cracks of the lining blocks [3].

One method of effectively resolving these problems is to fabricate blocks with closed pores in which the pore size is approximately 500 µm, which is 50 % less than for existing lining blocks. Thus, it is possible to create foamed glass that can enhance the durability against thermal shocks that occur during fires and simplifies the construction process by reducing the damage and destruction that occurs during construction. For normal foamed glass, a glass material is pulverized, and a carbon based blowing agent (or CaCO₃, Na₂CO₃, etc.) is added to create a mixed powder. This is sintered for a long time at a temperature of 900°C or more, and gas forms when the carbon blowing agent is oxidized into the CO₂ in the softening glass. From this reaction, porous foamed glass with closed pores is fabricated [4]. There has been active research on introducing new blowing agents that can lower the sintering temperature of existing foamed glass to reduce energy consumption and create uniform closed pores of approximately 500 µm.

Kim et al. [5] used glass powders to fabricate foamed glass and reported that a minimum sintering temperature of 1100–1200°C is needed. However, such sintering temperatures are very high for the industrial usage, and in terms of energy reduction, there is a need for achieving somewhat lower sintering temperatures and shorter sintering time. Lv et al. [6] employed carbon black with particles sizes of 0.074, 0.150, and 0.500 mm as a blowing agent and performed 1400°C sintering for 30 min at ramp up rates of 6, 8, and 10°C/min. They found the pore sizes of 0.5 mm, 0.8 mm, and 1.3 mm and reported that the pore size decreased as the particle size of the blowing agent decreased, making it possible to successfully create closed pores of 800 µm. However, the reality is that research on nanocarbon (NC) blowing agents is still insufficient. Kim et al. [7] varied the carbon blowing agent content from 0.1 to 1.0 wt% and examined the properties of foam glass. They reported that 0.2 wt% and 0.3 wt% were appropriate carbon contents.
However, there has been insufficient research on adding carbon blowing agent in larger amounts of up to 10 wt%.

Therefore, to fabricate foamed glass with 500 µm closed pores in the temperature range 700–900°C, in this study, we used nano-sized blowing agents and examined a new process that can lower the process temperatures below existing sintering process temperatures under process conditions that can lower the costs. In this study, we also examined the properties of the foamed glasses resulting from this new approach, including compressive strength and thermal conductivity.

2. Experimental procedure

To examine the properties of manufactured foamed glass as a function of the particle size of the glass starting material and the sintering temperature, we employed 35 nm-sized NC, 2 mm-diameter bulk glass composed of boron-free 82.64 wt%-SiO$_2$, 9.43 wt%-CaO, 4.91 wt%-MgO, 2.18 wt%-SO$_3$, and 0.84 wt%-Al$_2$O$_3$ as the raw material. A planetary ball mill (pulverisette 6, FRITSCH) was used to perform dry grinding on the prepared bulk glass and fabricate a uniform glass powder of less than 300 µm. NC was added to the pulverized glass powder at 2, 4, 6, 8, and 10 wt%. Isopropyl alcohol (IPA) was added, and ball milling was performed to mix it. The mixed sample was dried in an 80°C oven for more than 24 h to remove the solvent, and ball milling was performed again to create a mixed powder sample. To perform sample sintering, an electrical furnace (SK1700-B30, Thermotech Co.) was used to sinter the samples at 700°C, 750°C, 800°C, 850°C, and 900°C. The detailed conditions of the sintering temperatures are shown in Figure 1. The temperature was ramped up to 400°C at a rate of 3°C/min and maintained for 60 min. Then, it was increased at a ramp up rate of 10°C/min to the respective targeted maximum temperatures of 700°C, 750°C, 800°C, 850°C, and 900°C. It was maintained for 60 min and cooled at a rate of −1°C/min. To check the pore shapes of the sintered samples, 50 µl of H$_2$O was dropped on the specimen surface using a micropipette. After waiting for 1 min, the shape and height of the droplet were observed using a macro camera to verify whether it is an open pore or closed pore. Subsequently, the completed samples were polished with #400, #1000, and #2000 sand paper, and the microstructure and pore size of their cross sections were examined. The average pore size was determined from data of 100 pores based on 60x magnified images of the given samples.

An optical microscope (GIA x60, AX-10 ZEISS x500) was used to observe the samples. To check the porosity, an image analyzing program (iSolution DT x64(IMS digital)) was used to examine the surface pore area of the observation area of a 100x magnified optical microscope image. An Instron 3344 (INSTRON (Co.)) was used to determine the compressive strengths of the samples. The samples were cut into dimensions of 4 × 4 × 8 mm. To reduce the deviation in the measured values, three or more samples were measured, and the average values were recorded. A heat flow meter (HFM, NETZSCH (Co.)) was used to perform the thermal conductivity analysis to examine the insulation properties of the sintered samples. Measurements were recorded three times in an Ar atmosphere using a laser with a 600 µs pulse width at 260 V, and the average thermal conductivity values were measured.

3. Results and discussion

Figure 2 shows optical microscope images of the samples with no NC and with 10 wt% of NC were sintered at 750°C and 850°C, respectively. Figure 2(a) shows an image of the 750°C–0 wt% NC sample. It shows spherically formed closed pores that have an average pore size of 71.45 µm. Figure 2(b) shows an image of the 750°C–
10 wt% NC sample. It shows spherically formed closed pores that have an average pore size of 470.67 µm. There was a clear increase in pore size with the blowing agent content. Figure 2(c) shows the image of a sample fabricated by adding 850°C–0 wt% of NC. The fabricated sample had closed pores with an average pore size of 593.33 µm. Furthermore, as indicated by the arrows, it was found that there were different pore walls with thicknesses ranging from 160 to 32 µm along with micropores of approximately 40 µm inside the pore walls as indicated by a circle. Figure 2(d) shows the image of a sample fabricated by adding 850°C–10 wt% of NC. The fabricated sample had closed pores with an average pore size of 1066.33 µm. The pore size was twice as large as that of the sample with no NC as shown in Figure 2(c). Furthermore, similar to Figure 2(c), there were different pore walls with thicknesses ranging from approximately 200 to 480 µm as well as larger micropores of approximately 109 µm inside the pore wall as indicated by a circle. At the same temperature, larger closed pores were created as more NC was added. At 10 wt% NC, it was possible to obtain pores with an average size of 1066 µm. At the same NC content, larger closed pores were fabricated as the sintering temperature increased.

Figure 3 shows a graph that uses a log scale to show the changes in the closed pore size as a function of the NC content and sintering temperature. Here, the error bars are indicated by the minimum and maximum values for each sample. The pore size increased as the sintering temperature increased and as the NC content increased. When the NC content was 4 wt% or less, pores did not form at 700°C. The pores formed in proportion to the temperature beginning at 750°C. For the 700°C process, the temperature range was lower than the glass transition temperature, and this may be why the pores did not form. At the same sintering temperature, the size of the pores increased as the NC content blowing agent increased. When Lv et al. [6] used carbon as a blowing agent, the pores merged together after foaming occurred in the CO2 and CO gas that was created by the C + O2 → CO2 and 2C + O2 → 2CO reactions. In sintered bodies that included the NC blowing agent at 6 wt%, 8 wt%, and 10 wt%, similar pore sizes were observed at 700–850°C. At 900°C, the pore size rapidly increased. At temperatures above 850°C, the carbon that was added as the blowing agent displayed rapid blowing performance. This corresponds with the results reported by Lotov et al. [8] in which the pore size increased as the sintering temperature increased. When carbon was added at 6–8 wt% and sintered at 750°C, pores that were approximately 500 µm (Area “A”) were obtained. These results occurred for temperatures that were approximately 100°C less than the process conditions that resulted in the 1000 µm grade foamed glass (Area “B”) [9]. When the NC content was the same, the pore size increased as the sintering temperature
increased. This corresponds to the report by Lv et al. [6], who stated that when carbon was used as a blowing agent, the CO\textsubscript{2} and CO created during the sintering process experienced increased volume expansion owing to the increased temperature, forming large pores. In the sample with no added NC, the pores became larger as the sintering temperature increased. This occurred owing to the \( \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2 \) reaction within the glass starting materials even when there was no C present, as observed in a previous study by Kim et al. [10]. This has a bigger effect than the foam gas expansion caused by the \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \) reaction resulting from the carbon blowing agent, and it is believed that the inclusion of NC does not have a large effect until 4 wt%. Therefore, the low sintering temperature of 750°C and NC contents of 6–10 wt% were found to be favorable for the 500-µm grade closed pores, which are appropriate for industrial applications.

Figure 4 shows a graph of the porosity as a function of the NC content and the sintering temperature. The porosity increased as the NC content and the sintering temperature increased. At the same sintering temperature, the porosity increased as the NC content increased. This may be that because the \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \) and \( 2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \) reactions increased as NC content increased, which was added as the blowing agent, and there was a relative increase in the pores caused by the resulting CO\textsubscript{2} and CO, which increased the porosity. At the same NC content, the porosity increased as the sintering temperature increased. This increase in porosity with the increase in sintering temperature agreed with the results of the study by Lim.
et al. [11] in which porous SiC was made by adding aluminum to SiC ceramics. In that study, there was an increase in porosity with an increase in sintering temperature regardless of the presence of additives. Thus, it was possible to fabricate foamed glass with a porosity of 46–82 % by adjusting the NC content and the sintering temperature. In particular, it was possible to manufacture the glass so that the 60% porosity of the 500 µm area (Area "A") was not considerably reduced compared to the 70 % porosity of the existing 1000 µm area (Area "B").

Figure 5 shows the compressive strength decreased with increasing sintering temperature, and at the same sintering temperature, the compressive strength decreased with increasing NC content. At 750°C, the compressive strength was 2.95 MPa at a carbon content of 0 wt%, 2.84 MPa at 2 wt%, and 2.55 MPa at 4 wt%. This may have occurred because pores did not form when there was a small amount of NC used as the blowing agent and the sintering temperature was low, as observed previously. Additionally, the compressive strength was 2.33 MPa at a NC content of 6 wt%, 2.09 MPa at 8 wt%, and 1.79 MPa at 10 wt%. This corresponded to the changes in pore size and porosity observed in Figures 3 and 4. At 900°C and NC contents of 0 wt%, 2 wt%, 4 wt%, 6 wt%, and 8 wt%, the porosity trends corresponded to those observed in Figure 4. When the NC content was 10 wt%, the pores formed were of sizes approximately 5000 µm or more, as observed in Figure 3, and the compressive strength could not be measured. At the same NC content, the compressive strength decreased as the sintering temperature increased. Thus, the pore size and porosity increased as the sintering temperature increased as observed previously, as shown in Figures 3 and 4. The porosity of the samples with 500 µm pore sizes was found to be 68 % at a NC content of 4 wt% and 72 % at 6 wt%, 76 % at 8 wt%, and 68 % at 10 wt%. The compressive strength showed the same trend as the porosity, with 1.45 MPa at a NC content of 4 wt%, 1.25 MPa at 6 wt%, 1.28 MPa at 8 wt%, and 1.43 MPa at 10 wt%. According to these results, when the pore size was the same, the compressive strength decreased as the porosity increased, and this corresponds to the results reported by Gibson et al. [12]. They reported that the compressive strength of porous material can be expressed by Equation (1). In the formula, $\sigma$ is the strength of the porous material, $\sigma_0$ is the reference strength without pores, $b$ is a constant that depends on the pore characteristics and $P$ is the porosity. Thus, it shows a decrease in compressive strength as the porosity increases.

$$\sigma = \sigma_0 \exp(-bP)$$  \hspace{1cm} (1)

Gibson et al. [12], and Rice [13] expressed the failure stress of a porous material as shown in Equation (2). Where $\sigma_{IC}$ is the sample’s failure stress, $K_{IC}$ is the fracture toughness, $K$ is a constant, and $C$ is the pore size.

$$\sigma_{IC} = \frac{K_{IC}}{\sqrt{KC}}$$  \hspace{1cm} (2)

Equation (2) shows that the compressive strength decreases as the pore size increases. This trend in compressive strength as a function of porosity and pore size corresponds well with the results shown in Figure 5. The lining block for FGD, which is considered as an application in this study, must have closed pores and excellent compressive strength, in addition to being lightweight. In this experiment, all samples were found to have closed pores, but density, which is the main factor to be lightweight, increased as the

![Figure 5. Compressive strength of foamed glass with sintering temperature and carbon content.](image)
pores became smaller. For example, the pore size of the 750°C–2, 4 wt% sample was 100 µm, but the densities were 0.311 and 0.262 g/cm³, which were approximately three times as high as that of the sample with 500 µm pore size. Thus, a higher density indicates a greater weight and the material loses its usability as a lining block for FGD because of its reduced characteristic as a lightweight material. The excellent area was indicated as “A” as shown in the figure. Figure 5 shows a comparison of conditions A and B with approximately 500 µm pores and 1000 µm pores, respectively. Condition A shows greater than twice the compressive strength of condition B. Therefore, when the sample in the A area is manufactured at a lower firing temperature than the sample in the B area, it could improve durability when applied to the FGD chimney.

Figure 6 shows the thermal conductivity results according to sintering temperature. Chang et al [14] reported that the smaller the pore size at the same porosity, the lower the thermal conductivity becomes. In this study, however, the thermal conductivity did not show significant differences. This is considered to be because of the error resulting from the variations in the degree of dispersion and pore wall thickness of the large and small pores as a result of the sintering temperature and the addition of nano carbons as shown in Figure 2. Therefore, despite a slight difference in thermal conductivity between the A and B areas on comparing the condition of approximately 500 µm pores in A area and 1000 µm pores in B area, it was considered to be within the error range. When the thermal conductivities of thermal insulation are considered, it suggests that the foamed glass with 500 µm grade pores can act as a chimney refractory material, despite being manufactured at a lower temperature [15].

4. Conclusions
In this study, 2–10 wt% NC was added to glass material without boron and sintered at 700–900°C to produce foamed glass with closed pores. When NC was used as the blowing agent, it was possible to fabricate foamed glass with 500 µm grade pores at a sintering temperature that was 100°C lower than that used for existing 1000 µm grade foamed glass. The properties of the foamed glass with the 500 µm grade pores and the foamed glass with 1000 µm grade pores were compared, and it was found that it is possible to create samples with closed pores even though the sintering temperature was approximately 100°C lower. The pore size increased as the sintering temperature and the NC content increased, and it was possible to fabricate foamed glass with a variety of pore sizes for the temperature range 700–900°C. It was also possible to adjust the porosity between 46 and 82 %. A compressive strength of 1.25–1.45 MPa was observed in foamed glass with a pore size of approximately 500 µm. A compressive strength of 0.5 MPa was observed for the foamed glass with a pore size of approximately 1000 µm. This shows that the reduction in pore size resulted in an excellent compressive strength, which was more than twice that of the existing foamed glass. Regardless of the pore size, the thermal conductivity was less
than 0.28 W/m-K, indicating that both materials can be used as thermal insulation.

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