Preparation of high strength and low-cost glass ceramic foams with extremely high coal fly ash content

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Abstract. The success of recycling the molten blast furnace slag to glass fiber in industrial scale greatly encourage us to keep on seeking more environmental friendly applications from industrial waste. In this work, high strength and low-cost glass ceramic foams are prepared with extremely high coal fly ash content. The prepared glass ceramic foam sample introduced 89% coal fly ash and 6% CaCO₃, and sintered at 1150 °C has the best comprehensive properties, with the bending strength reaches 80.3 MPa, even though the bulk density is relatively high. The method is a good way to recycle the coal fly ash and the product will be used as a commercial building material to generate economic benefits.

1. Introduction
Recently, a yearly 20,000 tons glass fiber production line is successfully running in China for recycling the molten blast furnace slag. The first success in the industry scale greatly encourage us to keep on seeking more environmental friendly applications from industrial waste.

The coal-based energy structure in China generates more than 200 million tons of coal fly ash annual emission. However, the comprehensive utilization of it is only less than 40%, and among which, most of the fly ash are used for land filling which may endanger the environment and human beings.

The coal fly ash [1] can be recycled to glass-ceramics [2, 3], concrete [4], foam glass [5], etc. Among all the recycling methods, glass ceramic foam [6] is a type of high-quality and widely used building materials due to its excellent thermal insulation, sound absorption and lightweight [7] properties. Fernandes[8] prepared glass ceramic foams by using fly ash and sheet glass cullet, while the content of fly ash is only 20% and the compressive strength is below 1.8 MPa. Chen [5] produced low density foam glass with 70% fly ash content, and the compressive strength is 3.44 MPa. Compare to glass-ceramic [9], the strength of glass ceramic foams still can be greatly improved.

In this work, we aim to prepare high strength and low-cost glass ceramic foams directly from coal fly ash (>80%) by only adding small amount of foaming agent, and the product will be used as a commercial building supporting material.

2. Experimental Procedures

2.1. Materials
The chemical compositions (wt%) of the fly ash used in this work: 43.42 SiO₂, 26.76 Al₂O₃, 6.69 Fe₂O₃, 10.99 CaO, 1.22 MgO, 1.45 TiO₂, 2.73 SO₃, 0.73 Na₂O, 1.40 K₂O, 4.48 C and 0.14 others. The average particle size was between 0.2mm~0.3mm which is under sieve mesh 80.

In this work, we only introduced calcite as the foaming agent and Sodium carbonate as fluxing agent to prepare the glass ceramic foams. The samples with same composition were divided to 4 groups...
A, B, C, D which were sintered at 4 different temperatures 1100°C (group A), 1150°C (group B), 1200°C (group C) and 1250°C (group D). The composition and properties of samples in group B are shown in Table 1.

| Sample | Fly ash | CaCO₃ | Na₂O | Sintering temperature/°C | CTE/10⁻⁶·K⁻¹ | Bending strength/MPa | Apparent porosity/% |
|--------|---------|-------|------|--------------------------|---------------|----------------------|----------------------|
| B1     | 95      | 0     | 5    | 1150                     | 4.5±0.08      | 109.6±0.03           | 16.8±0.03            |
| B2     | 92      | 3     | 5    | 1150                     | 4.2±0.09      | 85.4±0.08            | 17.7±0.04            |
| B3     | 89      | 6     | 5    | 1150                     | 4.1±0.09      | 80.3±0.06            | 19.2±0.08            |
| B4     | 86      | 9     | 5    | 1150                     | 5.3±0.02      | 65.2±0.02            | 19.7±0.07            |
| B5     | 83      | 12    | 5    | 1150                     | 5.6±0.02      | 43.4±0.02            | 19.9±0.06            |

2.2. Samples Preparation
Firstly, the basic glass was prepared and wet mixed with the raw material in planetary ball mill for 60 min, then the powder was dried and compressed together with PVA glue under 1MPa. Afterwards, the formed raw materials (5×5×25mm) were heated to 450°C and kept 60 min to remove the glue. Secondly, based on the DSC curve of fly ash and decomposition temperature of CaCO₃, the samples were heated to 850°C at a rate of 5°C/min and holding 60 min for foaming and nucleating. Finally, the samples were sintered at different temperatures as 4 different groups for 60 for crystallization, and then slowly cooled down to room temperature.

2.3. Characterization Techniques
The morphology of the samples was studied by SEM (Hitachi S4800). The crystalline phases of samples were investigated by RIGAKU (D/Max-2550) X-ray Diffract meter. The bulk density was measured by the Archimedes method. The bending strength was tested by the universal material testing machine (20KNWDW3020). The thermal expansion coefficient was tested by high temperature horizontal dilatometer (PYC) and each final result represents the average value from five measurements.

3. Results and Discussion
3.1. Bulk Density
Results shown in Fig.1 indicate that both sintering temperature and foaming agent content can significantly affect the bulk density of samples. At the sintering temperature of 1100°C (Group A), the samples are still not sintered with obvious powers on the surface, and the bulk density is the lowest. When the sintering temperature reaches 1250°C (Group D), the samples are all melted with clear glass phase on the surfaces (Fig.1), and the bulk density is relatively low. For the Group B and Group C, the foaming and crystallization are processing well, and the bulk density decreases by the increase of sintering temperature. The elevating of temperature leads to the decreasing of viscosity, which is conducive for the growth of pores and lower the bulk density. It also can be seen in Fig.1 that, the increasing of CaCO₃ content accompanied by the decrease of the bulk density. The formation of pores in glass ceramic foams is directly related to emission of CO₂ decomposed from CaCO₃, thus the one with high CaCO₃ content is easily with high porosity which is the main reason to obtain the low bulk density.
Figure 1. Bulk density of samples as a function CaCO$_3$ content at different sintering temperatures. The digital photos show the corresponding sample with 6 % CaCO$_3$

3.2. Microstructure
The microstructure of samples in Fig.2 show that the foaming of both Group B and Group C are quite successful, while the pores have different diameters. Compared the samples in Group B, the sample with 6 %CaCO$_3$shows the best foaming state that most of the pores distribute homogeneously. Additionally, the sample with 3 %CaCO$_3$ is not sufficient for the foaming process, and the one with too much foaming agent (9 % CaCO$_3$), caused the increasing of inner pressure, may lead to the formation of large pores or even the burst of pores. The microstructure has a good correlation with bulk density in Fig.1. On the other hand, compared the samples with same CaCO$_3$ content of 6 % and different sintering temperatures, the sample sintered at 1200 °C shows less uniform pores distribution than at 1150 °C. At high sintering temperature, some of the small pores disappear or gather to become large pores for reducing surface energy[10], and some large pores are expanded being more irregular or generate intercommunicating pores. Theoretically, an ideal microstructure in glass ceramic foam must have a good balance between the glass viscosity, the surface energy and the gas pressure[11]. In this work, the CaCO$_3$ content and temperature are crucial. The sample with 6 % CaCO$_3$ and sintered at 1150 °C shows the best microstructure.
Figure 2. SEM morphology of samples. (a) 3% CaCO$_3$ sintered at 1150°C; (b) 9% CaCO$_3$ sintered at 1150°C; (c) 6% CaCO$_3$ sintered at 1150°C; (d) 6% CaCO$_3$ sintered at 1200°C

3.3 Bending Strength and Apparent Porosity
As shown in Table 1, with increasing CaCO$_3$ content, the bending strength decreases dramatically. The bending strength is consistent with the microstructure in Fig. 2 that the amount of foaming agent strongly affects the amount and size of the pores in glass ceramic foam and therefore influences the bending strength. In our opinion, with the increasing CaCO$_3$, the pore walls become thinner, and the microstructure becomes unstable, which might weaken the bending strength. The apparent porosity is calculated by water absorption (ISO 10545-3), and it is relatively small in this work. The bending strength and apparent porosity reaches a relative balance when CaCO$_3$ content is around 6%.

3.4 Thermal Expansion Coefficient (CTE)
The CTE of Group B samples is reported in Table 1. The CaCO$_3$ dependence of CTE is firstly decreasing from 4.5 to 4.1 $10^{-6}$·K$^{-1}$ (6%) and then increasing to 5.6 $10^{-6}$·K$^{-1}$. The pores inside the samples can ‘counterbalance’ part of the expansion, so that the CTE decreases at the beginning, while with more and more small pores merging to the big ones, the CTE is increasing again.
3.5. Crystalline Phase Analysis
The only crystalline phase inside the fly ash (Fig.3) is quartz, and the background is corresponding to glass phase. The main crystalline phases of B3 are Plagioclase ((Ca, Na)(Si, Al)₄O₈) and Albite (Na(Si₃Al)O₈). The crystalline phases inside the glass ceramic foams are the most important factor for achieving high bending strength [12].

4. Conclusions
In this work, high strength and low-cost glass ceramic foams are prepared with extremely high coal fly ash content. The sample B3 introduced 89% coal fly ash and 6% CaCO₃, which is sintered at 1150 °C, has the best comprehensive properties. The bending strength of sample reaches 80.3 MPa, the coefficient of thermal expansion is 4.1×10⁻⁶·K⁻¹, even though the bulk density is relatively high of 1.571 g·cm⁻³, and the apparent porosity is relatively low of 19.2%. The method is a good way to recycle the coal fly ash for environment protection and the product will be used as a commercial building material to generate economic benefits.

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