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Hydrothermal metallurgy for recycling of slag and glass

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Abstract. The authors have applied hydrothermal reactions to develop recycling processing of slag or glass. As an example, under hydrothermal conditions such as 200 ~ 300°C and 30 ~ 40MPa with H₂O, powders made of glass can be sintered to become solidified glass materials containing about 10mass% H₂O. When the glass containing H₂O is heated again under normal pressure, the glass expands releasing H₂O to make porous microstructure. H₂O starts to emit just above the glass transition temperature. Therefore, when we have a glass with low glass transition temperature, we can make low temperature foaming glass. The SiO₂-Na₂O-B₂O₃ glass is a candidate to be such a foaming glass. In this paper, we describe our recent trial on the fabrication of the low temperature foaming glass by using hydrothermal reaction.

1. Introduction

A large amount of slag is discharged from iron & steelmaking industries and mainly recycled for construction materials such as road bed materials. In addition, waste glass is also required to promote recycling by developing a reasonable recycling processes. Since slag and glass mainly consists of SiO₂, CaO, Al₂O₃, MgO, FeO etc, which are general components of ceramics materials, general sintering processes can be applied to produce some solidified materials from slag or glass. We have to, however, keep in mind that heating processes accompany energy consumption and sometimes CO₂ emission. Therefore, the authors have focused on the application of hydrothermal reactions to solidify the slag or glass powders to produce functional ceramic materials such as architecture materials etc.^{1,2)} Hydrothermal reaction occurs with liquid H₂O under high pressure, that is to say, water at 120 ~ 350 °C as shown in Fig.1. This temperature can be obtained from exhausted heat coming out of iron & steelmaking processes or waste melting furnace etc. The application of the hydrothermal reactions is one of ideal environmental-friendly processes to cope with recycling issues of slag as Jung et al. have pointed out^{3,4)} and they have already applied the hydrothermal reactions to solidify slag powder with some additives.

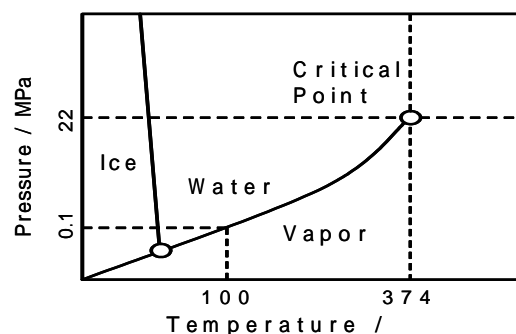


Figure 1. Phase diagram of H₂O.

The microstructure of molten slag or glass, which mainly consists of SiO_2 based network structure, is controlled by the addition of alkaline or alkaline-earth oxides to change chemical and physical properties such as basicity, viscosity etc. at high temperature. Under hydrothermal conditions, the microstructure of slag or glass might be controlled by H_2O , and this approach can be called "Hydrothermal Metallurgy".

Here, even when we can solidify glass or slag powder to make some materials, we are still required to add some additional functions to those solidified glass or slag materials. In order to equip more useful functions to those hydrothermally solidified materials, we have tried to make porous materials from slag or waste glass by applying hydrothermal reactions as described below. When we have porous glass or slag materials, those materials can be used as an insulator to control heat transfer, as a filter to remove impurities from polluted air or water, and furthermore as water reserve materials which can be applied to decrease temperature of wall or sidewalk by vaporizing H_2O absorbed in the porous structure of the materials in sunny days after H_2O is absorbed and kept during rainy days. Thus, if porous materials can be made from waste glass or slag by hydrothermal reactions, we may propose an environmental-friendly processing to create value-added materials to contribute largely to eco-society. The authors have been attempting to make various kinds of porous materials based on slag and glass. In this paper, we describe an example on fabrication of low temperature foaming glass by using "Hydrothermal Metallurgy"

2. Fabrication of low temperature foaming glass

Matamoros-Veloza et al.^{5,6)} dissolved H_2O in waste glass mainly composed of SiO_2 , Na_2O and CaO by hydrothermal synthesis and obtained a hydrated glass compact. When the prepared glass was heated, it started to expand and foam around 923 K with the release of water and became a porous material. The expansion of the glass is one of the reasonable approaches to make porous materials, but a foaming at a lower temperature would be beneficial. Since glass containing H_2O can be made at around 473K by hydrothermal reactions, it is to be desired that the foaming or expansion occurs at around the same temperature.

When the soda-silicate based glass was hydrothermally reacted, the constituents of the glass considerably influenced the water content of the glass under an identical hydrothermal condition. Moreover, it was found^{7,8,9)} that an increase in water content lowers the glass transition temperature as shown in Fig.2. For the fabrication of low temperature foaming glass, 63mass% SiO_2 - 27mass% Na_2O - 10mass% B_2O_3 glass, which exhibited adequate low glass transition temperature around 423K after the hydrothermal treatment as reported in the previous study^{7,8,9)}, was selected in the present work. The glass was subjected to the hydrothermal treatment at 523 K and its water releasing and foaming behavior with a heat treatment at 423 – 673 K was investigated¹⁰⁾.

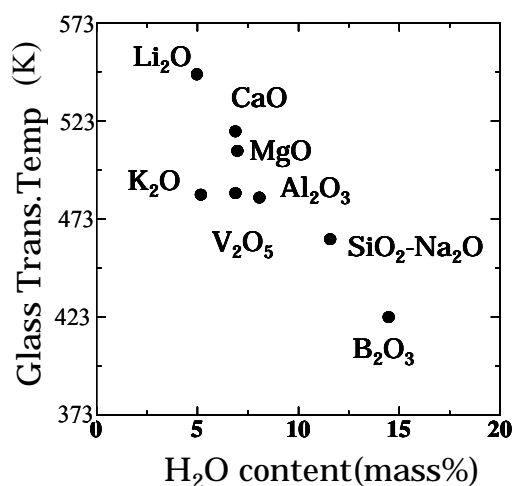


Figure 2. Relationship between glass transition temperature and H_2O content in 63mass% SiO_2 -27mass% Na_2O -10mass%MO glass (MO= Li_2O , CaO , MgO , K_2O , Al_2O_3 , V_2O_5 , B_2O_3).

3. Experimental

The original glass sample was prepared from reagent grade quartz, Na_2CO_3 and H_3BO_3 . These mixed powders corresponding to a composition of 63 mass% SiO_2 – 27 mass% Na_2O – 10 mass% B_2O_3 were melted in a Pt-20%Rh crucible at 1473 K for 3 h in air, and then rapidly cooled on a copper cooling block. The glass was subjected to a hydrothermal hot-pressing (HHP) technique. The experimental apparatus of HHP is shown in Fig.3. Pre-melted glass was ground and sieved at 63 μm . Glass powders were well-mixed with small amount of purified water and charged into the autoclave. After the mixture was pressed at 40 MPa, the autoclave was heated to 523 K within 20 min. and then immediately cooled to room temperature within the same time.

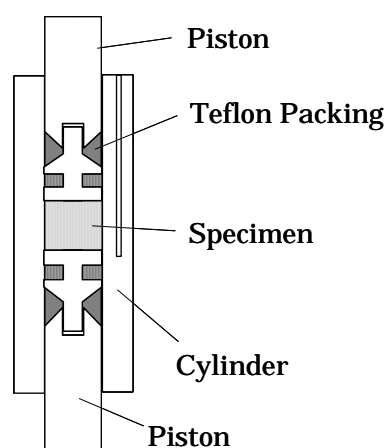


Figure 3. Hydrothermal hot pressing machine.

The HHP treated SiO_2 - Na_2O - B_2O_3 glass prepared above was cut into cubic blocks of almost 6 mm. Each block was placed on a platinum pan and heated in a horizontal electric resistance furnace controlled to 423 – 673 K in air for 5 min. The weight change in the sample was measured before and after the heat treatment. The apparent density of the sample after firing was determined by measuring its shape and weight.

4. Results and Discussion

To investigate the macroscopic change in the HHP treated SiO_2 - Na_2O - B_2O_3 glass, a block of the glass was heat-treated for 5 min. at 423 – 623 K in air. The samples after the heat treatment are shown in Fig.4.

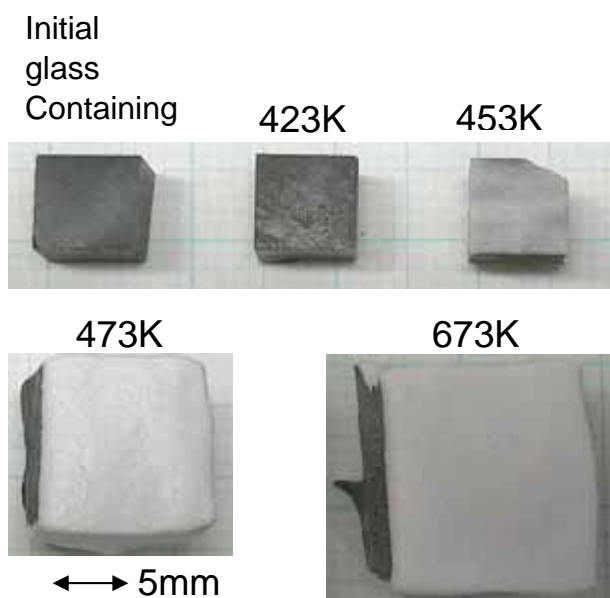


Figure 4. Change in macroscopic shapes of the HHP treated 63mass% SiO_2 - 27mass% Na_2O - 10mass% B_2O_3 glass after firing for 5 min. at 423 – 673 K.

Although no apparent change was observed when heated at 423 K, the sample heated at 453 K appeared to be whitened. Macroscopic expansion, namely foaming, of hydrated glass was observed for

the samples heated over 473 K, which corresponds to the starting temperature for water release observed by the TG-DTA analysis, in which Al_2O_3 powder was used as a reference. A higher heating temperature resulted in a larger expansion of the glass materials. Here, a low temperature foaming was successfully obtained ¹⁰⁾ compared with the previously reported temperature of around 923 K by Matamoros-Veloza et al. ^{5,6)} with soda-lime silicate glass, of which specimen size was 20mm diameter \times 10 mm height. It was confirmed by XRD analysis that the foamed glass at any temperature possesses the glass structure.

Apparent densities of the foamed glasses were determined from the sample shapes under the assumption of isotropic expansion. The apparent density decreases drastically at 473 K due to foaming, and continues to gradually decrease as the heating temperature increases. The lowest apparent density of 0.25g /cm³ was obtained when the heat treatment was conducted at 673 K although the density of the initial specimen was 2.6g /cm³. The weight loss was larger at a higher heating temperature, and the value of 11 % weight loss at 673 K was almost in accordance with the water content of the HHP treated glass. Those porous materials can be used for a filter to remove impurities in water or air.

5. Conclusion

Fabrication of low temperature foaming glass by using hydrothermal reaction was described as an example of the application of Hydrothermal Metallurgy. The HHP treated $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ glass was heated at 423 – 673 K in air to determine its macroscopic change by heating. A foaming behavior was observed even at 473 K and this foaming temperature was much lower than that of hydrated glass reported previously.

Acknowledgement

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