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Design of Porous Glass from By-Products in Materials Processing

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Introduction

Although a large amount of slag discharged from iron & steelmaking industries as well as waste melting furnaces has been recycled as construction materials, new processes for producing value-added materials have been required to promote the recycling of slag as well as waste glass. It is, however, very difficult to develop value-added materials from slag or glass because glass or slag is regarded as having low value of "Exergy" which indicates how valuable a material is. Exergy is defined in the following equation :

$$Exergy = \Delta H - T_0 \cdot \Delta S \quad (1)$$

where ΔH : the enthalpy, T_0 : room temperature, ΔS : the entropy of a material.

When a material has large ΔH and small ΔS, the exergy of the material is evaluated to be large. This means that the material is regarded as highly valuable and it is useful. Glass and slag are generally stable multi-component oxide materials. Oxides are more stable than metals, and thus the enthalpy of the oxides is less than that of metals. In addition, glass and slag are mixtures of many cations and anions, which means that their mixing entropy is very large. Therefore, glass and slag have very small exergy. This suggests that it is very difficult to create value-added materials from such glass and slag with low exergy in any recycling processing.

We assume in the above discussion that materials have infinite size and uniform structure. If "surfaces" or "interfaces" can be incorporated into a material structure, the material may gain additional valuable functions. For example, when we make porous glass or slag materials as shown in Figure 1, we can apply them for various ways owing to their surface phenomena, such as filter, adsorbent etc. The purpose of the present paper is to describe some examples of producing porous glass even from slag or waste glass.

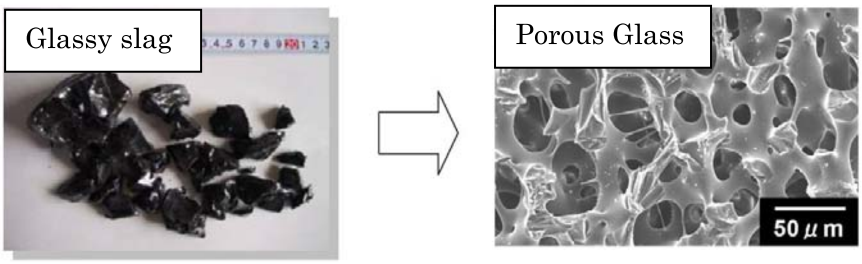

Figure 1 Making porous material from glass or slag with low value of exergy

1 Porous glass materials made by spinodal decomposition

Phase separation in glass refer to a phenomenon in which a single glass phase separates into two or more glass phases with different compositions in heat-treatments. Some experimental studies[1,2] have been carried out on the occurrence of the phase separation in various oxide systems. To create value-added functional glass materials using silicate slag discharged from metallurgical and ash melting processes etc., the authors have focused on and investigated the phase separation in multi-component oxide glasses containing fundamental components in slag[3,4]. For instance, spinodal decomposition as one phenomenon of phase separation forms interconnected microstructure in glasses, and porous glasses are produced by dissolving one of the separated glass phases with acid solution as described in Fig.2. Since the porous glasses have three-dimensionally interconnected porous structures, they are expected to have widespread applications, for example as filters to trap impurities in water. Thus, slag may be transformed into value-added functional glass materials using the phase separation in oxide glasses.

To generate phase separation in glass from slag, the composition ranges for metastable immiscibility as well as spinodal decomposition need to be evaluated for multi-component slag systems. For multi-component oxide systems such as slag systems, it is difficult to predict metastable immiscibility empirically. Therefore, it is necessary to perform a thermodynamic evaluation to determine the phase separation in multi-component oxide systems.

The authors attempted to predict the composition ranges for metastable phase separation and spinodal decomposition in the SiO_2-CaO-MgO-5mol%Na_2O system by calculating the composition dependence of the Gibbs energy curves in the super-cooled liquid phase as shown in Fig.3. In addition, Figure 4 shows one example of micro-structure in spinodal decomposition in the SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 system and porous structure obtained from leaching of one of the separated phases in the spinodal decomposition.

Figure 2 Concept of formation of porous glass materials from spinodal decomposition

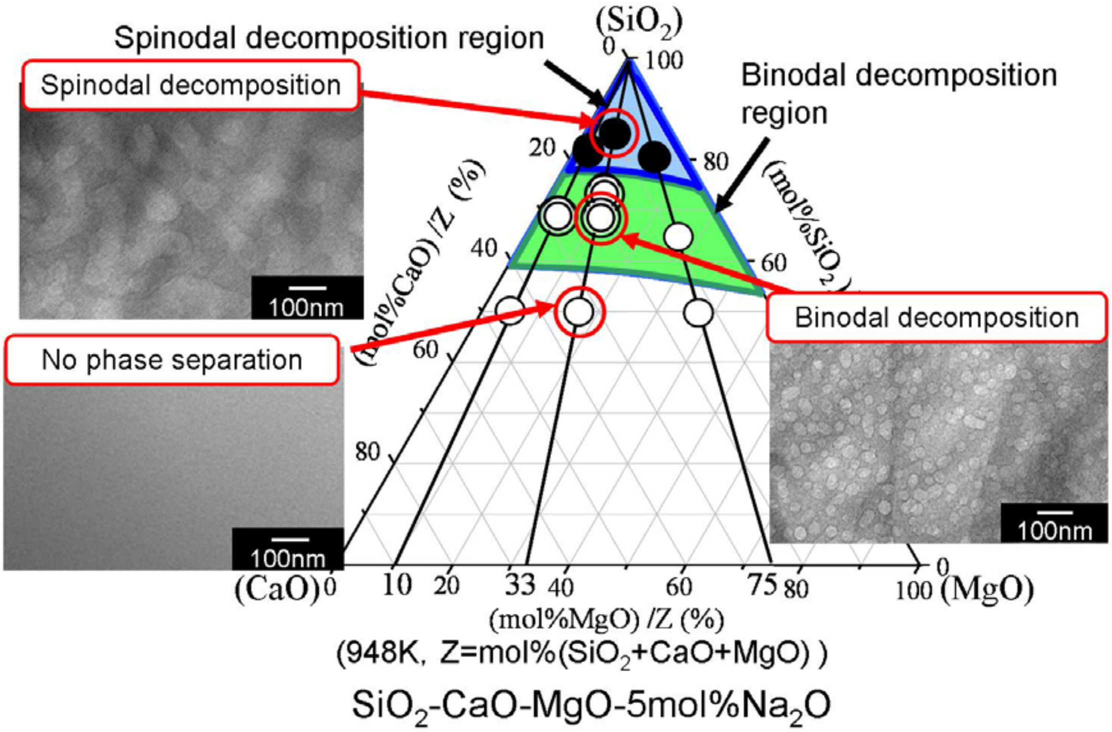

Figure 3 Comparison of thermodynamic calculation of phase decomposition regions with the experimental observation of micro-structures in various composition regions in SiO_2-CaO-MgO-5mol%Na_2O systems

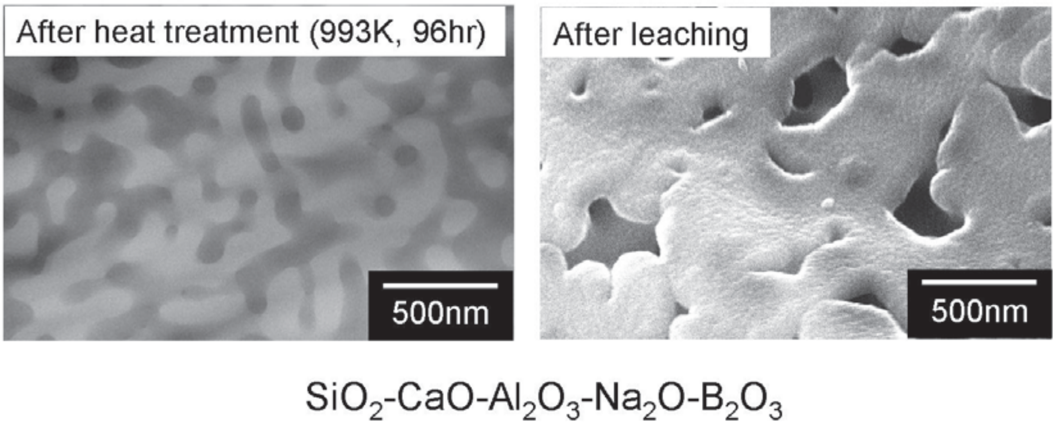

Figure 4 TEM observation of micro-structures of spinodal phase decomposition and porous structure obtained from leaching of one of the decomposition phases in SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 systems

2 Porous glass materials made by hydrothermal reaction

To make porous materials from slag or glass from the view point of no emission of CO_2 and low energy consumption, the authors have focused on the application of hydrothermal reactions to produce functional materials. Hydrothermal reactions occur for liquid H_2O under high pressure, that is to say, water at 120～350 oC as shown in Fig.5. This temperature can be obtained from exhausted heat coming out of iron & steelmaking processes or a waste melting furnace etc.

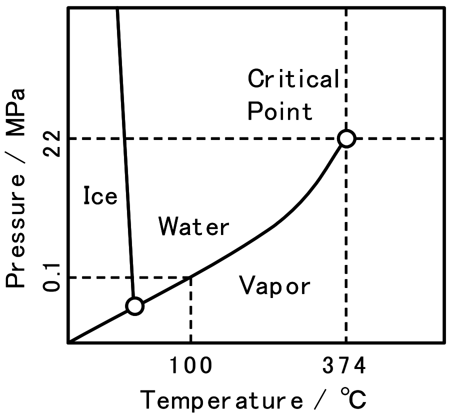

Figure 5 Phase diagram of H_2O

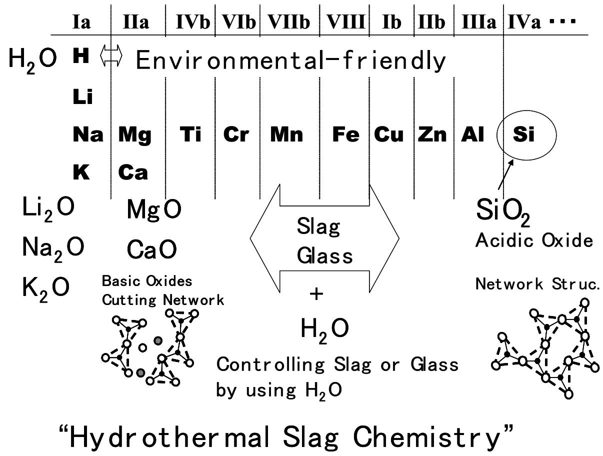

Figure 6 Concept of "Hyrothermal Slag Chemistry"

The application of the hydrothermal reactions is an environmental-friendly method for coping with issues of recycling slag as Jung, Hashida, Ishida, Yamasaki et al. have pointed out [5] and they have already applied the hydrothermal reactions to solidify slag powder with the use of some additives. The microstructure of molten slag, which mainly consists of a SiO_2 based network structure, is controlled by the addition of alkaline or alkaline-earth oxides to change the chemical and physical properties of molten slag such as basicity and viscosity in iron & steelmaking processes at high temperature. This scientific field refered to as "Slag Chemistry". Under hydrothermal conditions, the microstructure of slag might be controlled by H_2O and we have named this new approach "Hydrothermal Slag Chemistry" as shown in Fig.6[6].

3.1 Sintering of slag or glass powder at low temperature around 2500C by hydrothermal reaction

We have used two kinds of experimental apparatuses for hydrothermal reactions. One of them is a "Hydrothermal Hot Pressing (HHP)" machine, and the other is a normal autoclave. Figure 7 shows the schematic diagram of a hydrothermal hot pressing machine designed by Yamazaki et al.[5]. After mixing some amounts of water and slag powders, we set a sample between the pistons in the autoclave cylinder of the hot pressing machine. We applied high pressure of about 40MPa mechanically to the sample, and then heated the sample up to 250-350 oC to react the materials in hydrothermal conditions.

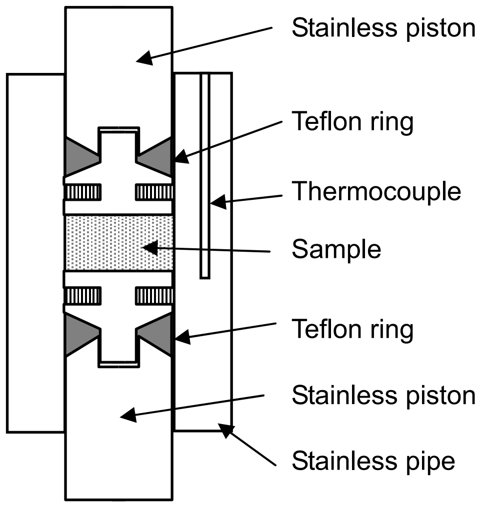

Figure 7 Schematic diagram of Hydrothermal hot pressing (HHP) machine

Figure 8 shows an example of the change in microstructure of SiO_2-Na_2O based glass powders with the addition of H_2O during hydrothermal reactions. As the holding time under the hydrothermal condition (300 oC, 30MPa) increased, it was found that the glass particles reacted with H_2O and the diameters of the particles decreased gradually.

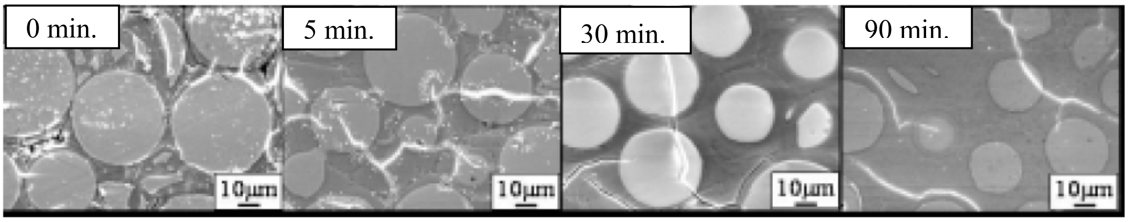

Figure 8 Progress of hydrothermal reaction of glass particles with H2O

Figure 9 shows two examples of solidified slag in dense (a) and porous (b) ceramics from hydrothermal hot pressing of blast furnace slag.

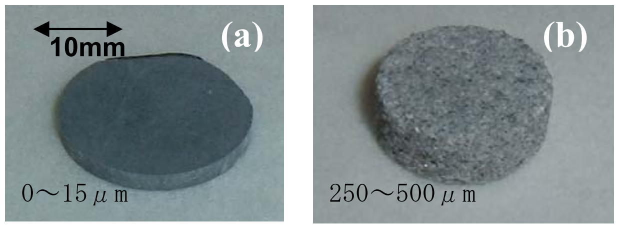

Figure 9 Examples of solidified slag after hydrothermal hot pressing of fine powders (a) and course powder (b) of blast furnace slag

3.2 Emission of H_2O from glass containing H_2O prepared by hydrothermal reactions to create porous glassy materials.

Figure 10 shows an example of microstructure in glass material (63mass% SiO_2-27mass% Na_2O-10mass%B_2O_3) after hydrothermal hot-pressing (a) and the material after H_2O release (b)[7]. In the sample after hydrothermal hot-pressing, H_2O dissolved into glass particles to form a reaction phase with H_2O around the glass particles. The sample after H_2O release has a porous structure as shown in Fig.15(b).

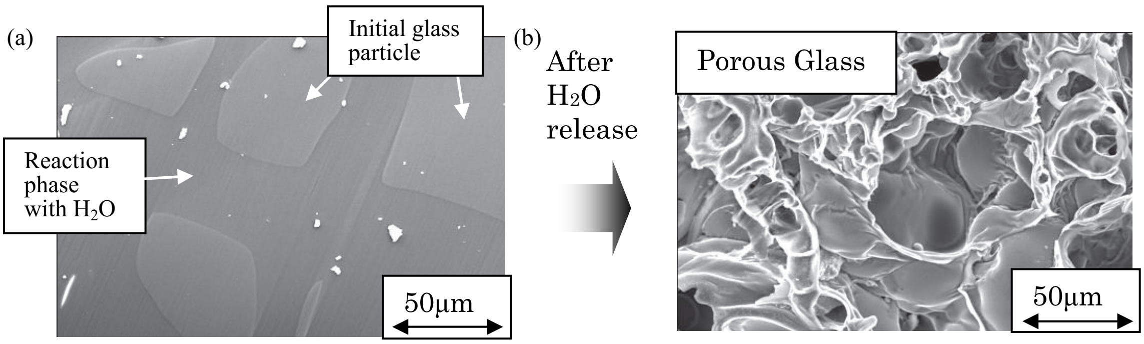

Figure 10 SEM images of (a) microstructure in glass materials after hydrothermal hot-pressing and (b) porous structure after water release

Matamoros-Veloza et al. [8] introduced water to waste glass mainly composed of SiO_2, Na2O 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. For the practical use of foaming glass, however, a foaming behavior at a lower temperature would be beneficial. For the fabrication of low temperature foaming glass, the above-mentioned 63mass%SiO_2-27mass%Na_2O-10mass%B_2O_3 glass, which exhibited adequately low glass transition temperature around 453K after the hydrothermal treatment [9], was subjected to hydrothermal treatment at 523 K and its water releasing and foaming behavior with heat treatment at 423 – 673 K was investigated [9,10].

Finally, we observed macroscopic expansion, i.e., foaming, of hydrated glass for samples heated in excess of 473 K as shown in Fig.11. Higher firing temperature resulted in a larger expansion of the glass materials. Here, a low temperature foaming was successfully achieved at around 473K [9,10], which was a lower temperature than the foaming temperature previously reported by Matamoros-Veloza et al. of 923K [8] using soda-lime silicate glass. The lowest apparent density of 0.25g /cm3 was obtained when the heat treatment was conducted at 673 K.

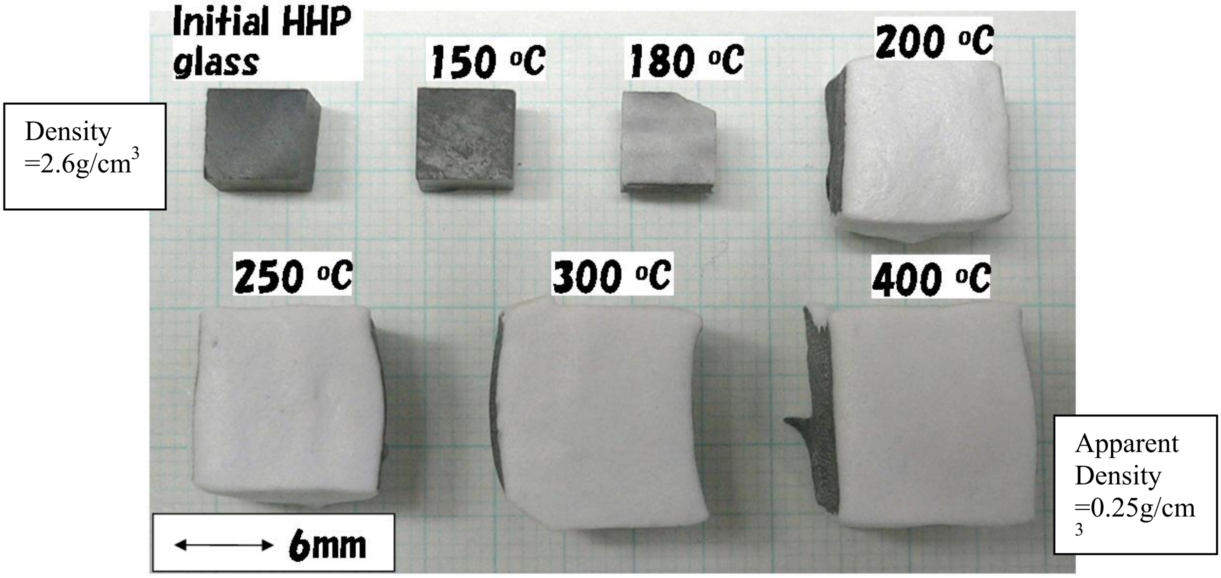

Figure 11 Expansion of glass containing H_2O by Hydrothermal Hot Pressing after re-heating at various temperatures

4 Conclusion

Some examples were explained to produce porous materials even from slag or glass. From the view point of "exergy", it has been considered very difficult to convert slag or glass to value-added materials; however, if we could convert slag or glass to porous materials, then we could have a new way of using them in an eco-society. In particular, if we could use H_2O in slag or glass as an "oxide", we may be able to develop a new technology or materials. The use of a hydrothermal reaction may be one of approach to achieve this goal. *(Professor, Osaka University)*

References

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