DESIGN OF POROUS GLASS & SLAG MATERIALS AND ITS APPLICATION TO REFINING

Toshihiro Tanaka, Takeshi Yoshikawa & Masanori Suzuki
Osaka University, Japan

ABSTRACT

Porous materials can be used to absorb impurities from liquids or gases and purify them. For example, molten slag can penetrate into small capillary tubes in solid CaO, along with impurities such as P_2O_5 and CaS. The latter are fixed on the inner surface of the capillaries as it happens in de-phosphorization or de-sulfurization processes in iron & steelmaking. Chemical reactions with solid phases are generally believed to be very slow due to slow diffusion in the solid phase. However, the above impurities are absorbed quickly by capillary forces and they are removed from molten steels. We refer to this procedure as "Capillary Refining".

In addition to solid, porous CaO, we can make porous materials from slag and waste glass.

In this paper, the following topics on the design of porous materials are presented:

- *Application of spinodal phase separation in super-cooled molten slag or glass to make porous material and*
- *Application of hydrothermal reactions to make porous slag or glass materials.*

These porous micro-structures are formed on the basis of self-organized phenomena; these materials have a three-dimensional, interconnected porous structures. Because of this, they can have widespread application, such as filters to trap impurities in water or air or as insulators to control heat transfer.

INTRODUCTION

Porous materials can be used to absorb impurities from liquids or gases and purify them. For example, molten slag can penetrate into small capillary tubes in solid CaO, along with impurities such as P_2O_5 and CaS. The latter are fixed on the inner surface of the capillaries as it happens in de-phosphorization or de-sulfurization processes in iron & steelmaking. Chemical reactions with solid phases are generally believed to be very slow due to slow diffusion in the solid phase. However, the above impurities are absorbed quickly by capillary forces and can be removed from molten steels. We refer to this procedure as *Capillary Refining* [1, 2]. Thus, there is the possibility of using the surface phenomena of porous materials, such as capillary force, adsorption, etc., to develop new materials or for materials processing.

Although a large amount of slag from the iron & steelmaking industries has been recycled as construction materials, new processes are required to promote the recycling of slag and waste glass and generate value added products. However, this is very difficult to do, since glass and slag are regarded as having a low *Exergy* value. Exergy indicates how valuable a material is and is defined as:

$$Exergy = \Delta H - T_0 \cdot \Delta S \tag{1}$$

When a material has large ΔH and small ΔS, the exergy of the material is 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 pure metals; thus, the enthalpy of 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 little 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.

In the above discussion, we assume that materials have an infinite size and a 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 may apply them in various ways because of their surface phenomena, such as capillary forces.

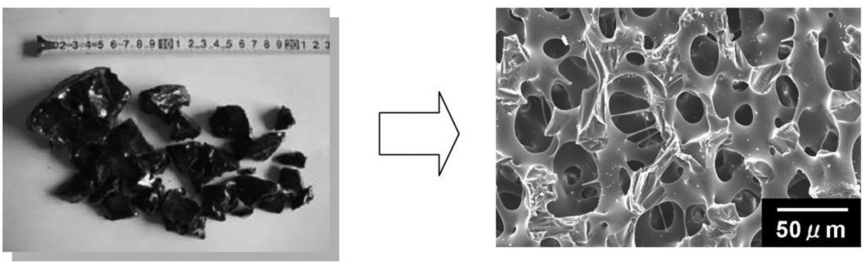

Figure 1: Making porous material from glass or slag with low value of exergy

The purpose of the present paper is to describe some of our research on the application of porous materials in the refining process in iron & steel making technology. Also, we present some examples on the production of porous materials from slag or glass.

CAPILLARY REFINING

There has been much research work pursuing highly efficient dephosphorization (De-P) and desulphurization (De-S) procedures of liquid iron alloys produced when using small amounts of highly reactive De-P and De-S fluxes in order to reduce the amount of slag in iron & steelmaking. To this effect, the present authors have studied interfacial phenomena related to De-P and De-S refining with solid CaO.

Solid CaO has many small capillary tubes, which are usually produced by CO_2 release during the calcination of $CaCO_3$. One of the major interfacial phenomena between liquid and solid phases is the penetration of liquid into small porosities in the solid, i.e.,: capillary phenomena. When the solid surface is wetted by a liquid, the latter is absorbed quickly into capillary tubes, as shown in Figure 2. In this manner, impurities in the liquid phase can be carried by the liquid phase and then fixed on the walls of the capillaries. Thus, capillary phenomena can serve as refining means to remove the impurities from the liquid. Molten slags containing P and S have good wettability with solid CaO and as a result, P and S may be removed from molten slags as shown in Figure 3. We have named this procedure as *Capillary Refining* [1, 2]. In the present paper, we describe some examples of the application of Capillary Refining to the De-S of liquid iron alloys.

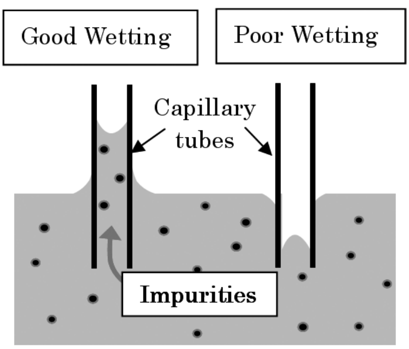

Figure 2: Capillary phenomenon. Absorption of liquid with impurities into capillary tubes

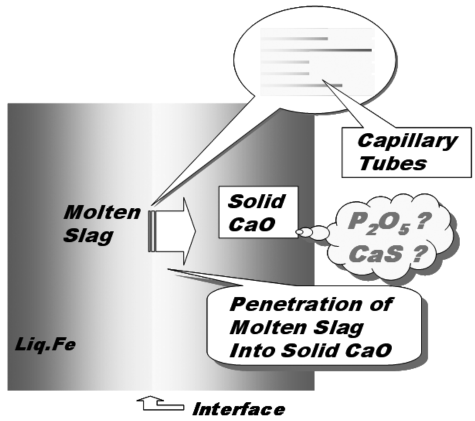

Figure 3: Concept of *Capillary Refining* to De-P and De-S of Liquid Fe

CAPILLARY REFINING AND DE-SULPHURIZATION OF LIQUID Fe

The authors have developed techniques for making solid CaO with a porous microstructure suitable for capillary refining. Figure 4 shows an example of a micro-structure of CaO obtained from $Ca(OH)_2$ powder bound with an organic material. The resulting microstructure has a three- dimensionally interconnected pore system, such as it exists in tissue paper.

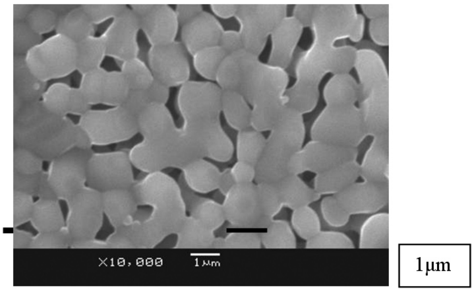

Figure 4: Microstructure of solid CaO suitable for capillary refining

In the experiments on the application of capillary refining to desulphurization of liquid iron alloys, we used molten CaO-SiO_2–MgO-35mass%Al_2O_3 slag at around 1723 K as shown in Figure 5. To this effect, the slags were previously equilibrated with pure, solid CaO; maintaining a high CaO activity in slag is essential for De-P and De-S reactions. Also, such slags have been reported by Iwase et al. to have a high sulfide capacity [3].

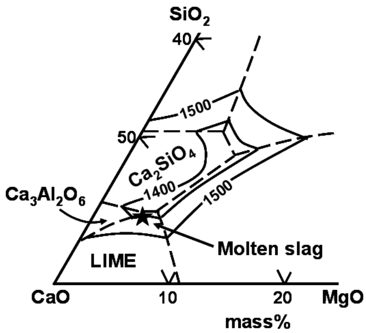

Figure 5: Phase diagram of CaO-SiO_2-MgO–35%Al_2O_3 [3]

In the present work, we desulphurized hot metal by capillary refining as follows: an iron sample saturated with carbon containing sulfur was melted in a graphite crucible. Following this step, a CaO-SiO_2-MgO–35%Al_2O_3 slag was melted on the surface of the liquid iron. De-S was carried out by attaching a solid CaO block with a porous structure to the molten slag in order to draw the slag into the capillary pores. The CaO block containing slag was then removed and a cross section specimen observed with an electron probe micro analyzer.

As indicated in Figure 6, S-containing molten slag penetrated into the capillary tubes in the solid CaO and reached the front of the penetration area, showing that we can carry out capillary refining for the De-S of hot metal using solid CaO with an adequate porous structure.

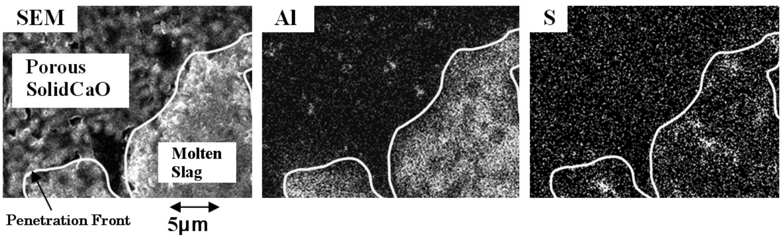

Figure 6: Experimental results for the penetration of CaS containing molten slag into solid CaO with a porous microstructure

SPINODAL DE COMPOSITION

Phase separation in glass refers to a phenomenon in which heat-treatment of a single glass phase leads to its separation into two or more glass phases with different compositions. There is some experimental studies on the occurrence of such phase separations in oxide systems [4, 5].

The authors investigated phase separation phenomena in oxide glasses containing essential slag components in order to create value-added glass materials from metallurgical processes [6, 7].

For instance, spinodal decomposition is a phenomenon of phase separation that forms interconnected microstructures in glasses. Following this, porous glasses can be produced by dissolving one of the glass phases with an acid solution, as described in Figure 7. Since the porous glasses have 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 by using a phase separation in oxide glass systems.

The composition ranges for metastable immiscibility as well as spinodal decomposition need to be evaluated in order to enhance phase separation in multi-component systems. It is difficult to empirically predict metastable immiscibility. Therefore, it is necessary to perform a thermodynamic evaluation to determine phase separation conditions 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 Figure 8. In addition, Figure 9 shows one example of micro-structure created by spinodal decomposition in the SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 system, followed by leaching of one of the phases separated on decomposition.

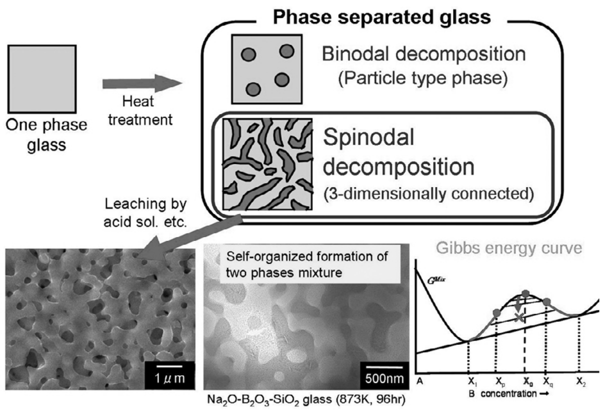

Figure 7: Concept for the formation of porous glass materials by spinodal decomposition

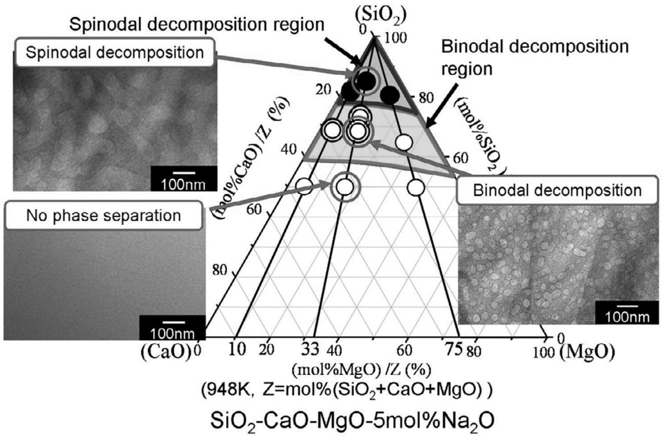

Figure 8: Comparison of thermodynamic calculation of phase decomposition regions with the experimental observation of micro-structures in various composition regions in the SiO_2-CaO-MgO-5mol%Na_2O system

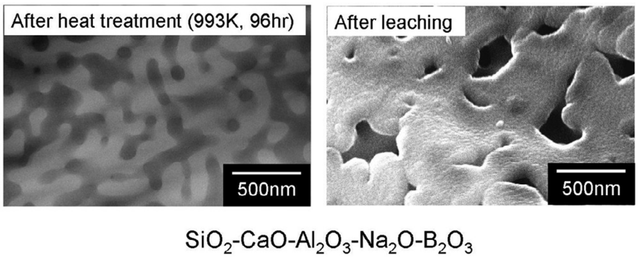

Figure 9: TEM observation of micro-structures of spinodal phase decomposition and porous structure obtained from leaching of one of the decomposition phases in SiO_2-CaO-Al_2O_3-Na_2O-B_2O_3 systems

POROUS GLASS MATERIALS MADE BY HYDROTHERMAL REACTIONS

The authors have also studied the application of hydrothermal reactions to produce to make porous materials from slag or glass. Hydrothermal reactions occur for liquid H_2O under high pressure, that is to say, water at 120-350°C as shown in Figure 10. This temperature can be obtained from exhaust heat from iron & steelmaking processes or from a scrap melting furnace, etc.

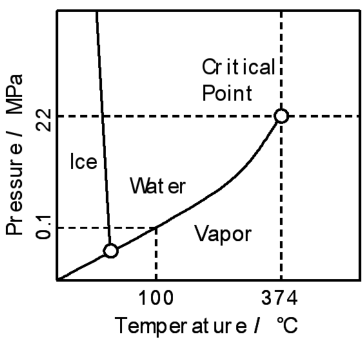

Figure 10: Phase diagram of H_2O

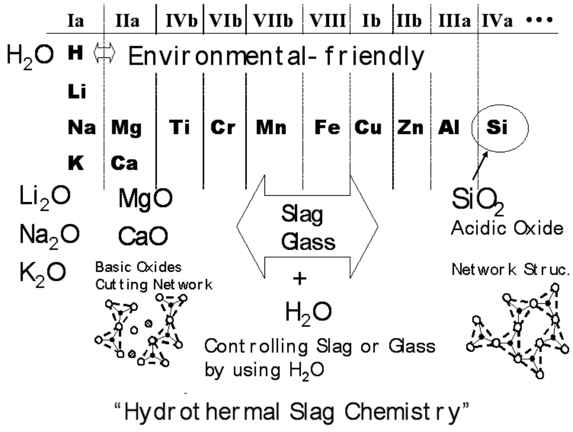

Figure 11: Concept of *Hydrothermal Slag Chemistry*

The application of hydrothermal reactions is an environmental-friendly method for recycling slags, as Jung, Hashida, Ishida, Yamasaki *et al.* have pointed out [8]. They have already applied such 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 and can be controlled by the addition of alkaline or alkaline-earth oxides to change its chemical and physical properties. This scientific field is usually referred to as *Slag Chemistry*. The microstructure of slags can also be changed by hydrothermal treatments; we have named this new approach as *Hydrothermal Slag Chemistry* as shown in Figure 11 [9].

Sintering of Slag or Glass Powder by Hydrothermal Reactions at Low Temperature (~250°C)

We have used two kinds of apparatuses for hydrothermal reactions. One of them is a *Hydrothermal Hot Pressing (HHP)* machine, and the other one is a normal autoclave. Figure 12 shows the schematics of a hydrothermal hot pressing machine designed by Yamazaki *et al.* [8]. After mixing some amount of water and slag powders, a sample is set between the pistons in the autoclave cylinder of the hot pressing machine. We applied a pressure of about 40 MPa to the sample, and then heated the sample up to 250-350°C to react the materials in hydrothermal conditions.

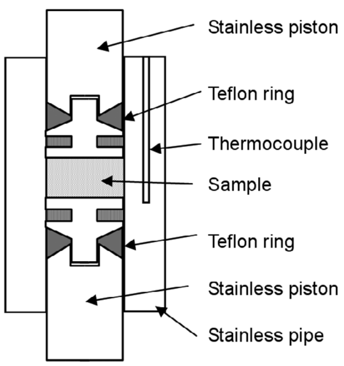

Figure 12: Schematic diagram of Hydrothermal hot pressing (HHP) machine

Figure 13 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°C, 30MPa) increased, it was found that the glass particles reacted with H_2O and the diameters of the particles decreased gradually.

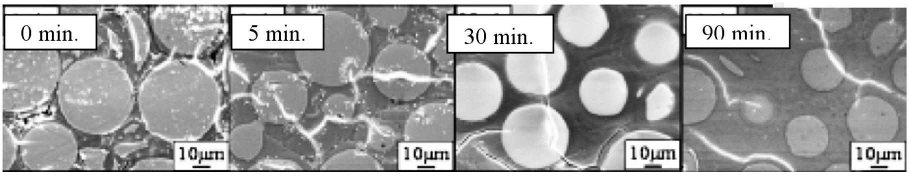

Figure 13: Progress of hydrothermal reaction of glass particles with H_2O

Figure 14 shows two examples of solidified slag in dense (a) and porous (b) ceramics from hydrothermal hot pressing of blast furnace slag.

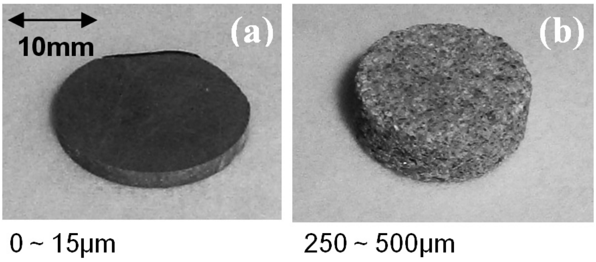

Figure 14: Examples of solidified slag after hydrothermal hot pressing of fine powders (a) and coarse powder of blast furnace slag (b)

Emission of H_2O from H_2O-containing Glass Prepared by Hydrothermal Reactions

Figure 15 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) [10]. 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 Figure 15(b).

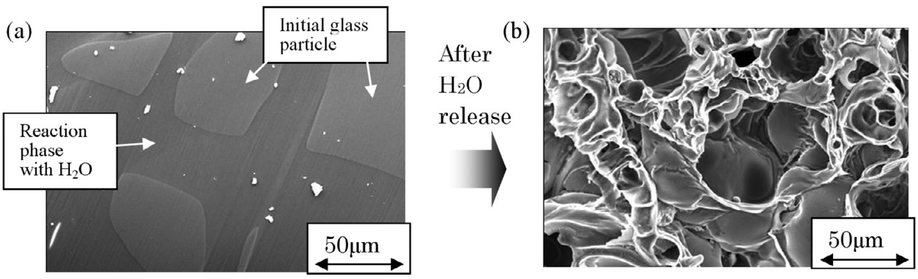

Figure 15: SEM images of (a) microstructure in glass materials after hydrothermal hot-pressing and (b) porous structure after water release

Matamoros-Veloza *et al.* [11] introduced water by hydrothermal synthesis to waste glass mainly composed of SiO_2, Na_2O and CaO and obtained a hydrated glass compact. When this prepared glass was heated, it started to expand and foam around 923 K, released water and became a porous material. However, for the purpose of foaming glass, a lower temperature would be beneficial. To this effect, the above-mentioned 63 mass%SiO_2-27-mass%Na_2O-10mass%B_2O_3 glass was tested. It had exhibited an adequately low glass transition around 453 K after the hydrothermal treatment [9]. It was now subjected to hydrothermal treatment at 523 K and its water releasing and foaming behavior with heat treatment at 423 – 673 K was investigated [12, 13].

Finally, we observed macroscopic expansion, i.e., foaming, of hydrated glass for samples heated in excess of 473 K as shown in Figure 16. Higher firing temperature resulted in a larger expansion of the glass materials. Here, a low temperature foaming was successfully achieved at around 473 K [12, 13], a lower temperature than that previously reported for soda-lime silicate glass by Matamoros-Veloza *et al.* (923 K) [11] The lowest apparent density of 0.25g /cm^3 was obtained when the heat treatment was conducted at 673 K.

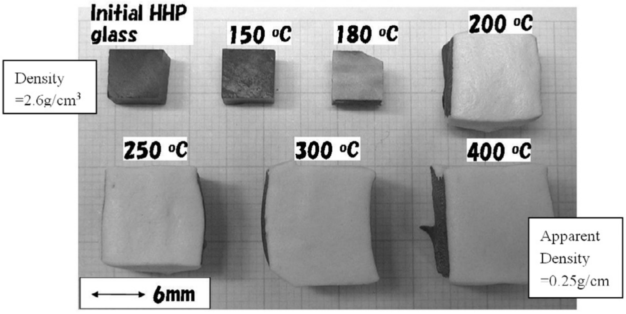

Figure 16: Expansion of glass containing H_2O by Hydrothermal Hot Pressing after re-heating at various temperatures

CONCLUSIONS

The concept of Capillary Refining of De-S reactions in liquid Fe was described as an example of the application of porous materials. Porous materials can be used as filters to remove impurities in liquids or gases, insulators for controlling heat transfer and so on. In addition, some examples were given for the production of porous materials 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 approach to achieve this goal.

NOMENCLATURE

ΔH = The enthalpy.
T_0 = Room temperature.
ΔS = Entropy of a material.

ACKNOWLEDGEMENTS

This study was partially supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES

Tanaka, T., Hara, S., Oguni, R., Ueda, K. & Marukawa, K. (2001). *Application of Capillarity of Solid CaO to Dephosphorization of Hot Metals*. ISIJ International 41, pp. S70-S72. [1]

Tanaka, T., Ueda, M., Omiso, Y. & Marukawa, K. (2006). *Application of Capillary Refining to De-P and De-S of Hot Metals*. Proc. ASIA STEEL International Conf. 2006, Japan, pp. 460-463. [2]

Hayakawa, H., Hasegawa, M. & Iwase, M. (2005). Committee of Steelmaking Processing, JSPS, Report No. 19-12158, IV-29. [3]

Burnett, D.G. & Douglas. R.W. (1970). *Liquid-liquid Phase Separation in the Soda-lime-silica System*. Physics and Chemistry of Glasses 11, pp. 125-135. [4]

Nakashima, T. & Kuroki, Y. (1981). *Effects of Composition and Heat Treatment on the Phase Separation of Na_2O-B_2O_3-SiO_2-Al_2O_3-CaO Glass Prepared from Volcanic Ashes*. Nippon Kagaku-kaishi, 8, pp. 1231-1238. [5]

Suzuki, M. & Tanaka, T. (2006). *Prediction of Phase Separation in Silicate Glass for the Creation of Value-Added Materials from Waste Slag*. ISIJ International 46, pp. 1391-1395. [6]

Suzuki, M. & Tanaka, T. (2008). *Composition Dependence of Microstructures formed by Phase Separation in Multi-component Silicate Glass*. ISIJ International 48, pp. 405-411. [7]

Jing, Z., Ishida, E. H., Jin, F., Hashida, T. & Yamasaki, N. (2006). *Influence of Quartz Particle Size on Hydrothermal Solidification of Blast Furnace Slag*. Ind. Eng. Chem. Res. 45, pp. 7470-7474. [8]

Tanaka, T. & Yoshikawa, T. (2008). *Application of Hydrothermal Reaction to Recycling of BF Slag and Waste Glass*. Proc. of SCANMET III, Lulea, Sweden, pp. 83-92. [9]

Nakamoto, M., Lee, J., Tanaka, T., Ikeda, J. & Inagaki, S. (2005). *Use of Slag Containing Water as Lubricant in High Straining Rolling for Ultrafine-grained Steels*. ISIJ International 45, pp. 1567-1571. [10]

Matamoros-Veloza, Z., Yanagisawa, K., Rendon-Angeles, J. C. & Yamasaki, N. (2002). *Preparation of Porous Materials from Hydrothermal Hot Pressed Glass Compacts*. J. Mater. Sci. Lett. 21, pp. 1855-1858. [11]

Sato, S., Yoshikawa, T., Nakamoto, M., Tanaka, T. & Ikeda, J. (2008). *Application of Hydrothermal Treatment on BF Slag and Waste Glass for Preparing Lubricant Materials in High Strain Rolling for Ultrafine-grained Steel Production*. ISIJ International 48, pp. 245-250. [12]

Yoshikawa, T., Sato, S. & Tanaka, T. (2008). *Fabrication of Low Temperature Forming Glass Materials Using*. ISIJ International 48, pp. 130-133. [13]