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Note

Preparation of Porous Ceramics by the Hydrothermal Reaction of Blast Furnace Slag for Use in a Water-retentive Material

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1. Introduction

Blast furnace (BF) slag is the greatest by-product in iron- and steelmaking processes. Although most is recycled in the raw materials for roadbeds, cements and concrete aggregates, new processes for producing more valuable materials are demanded. Recycling BF slag through a high temperature treatment based on melting or sintering is generally attempted because of its major components of ceramic materials such as SiO_2, CaO, Al_2O_3 and MgO, but it may not be feasible from the view point of the energy consumption. Therefore, the authors have focused on the application of hydrothermal reactions to the slag. Under a hydrothermal condition, materials are exposed to a high pressurized water vapor and/or a high temperature aqueous solution. It is beneficial that the reaction takes place at a temperature ranging from 373 to 623 K that can be controlled with the industrial waste heat. Hydrothermal treatments of BF slag have been applied in the production of heat storage material and high strength building material with additives.[1–4] In addition, the authors have studied the hydrothermal reaction of the slag for preparing functional materials.[5–7]

On the other hand, water-retentive material has been of interest owing to its effect of reducing the urban heat island phenomenon and its use in pavements and roofs has become more widespread. The material must have sufficient porosity, an affinity with water to contain it within, and an excellent mechanical property. It was clarified by previous research that the hydrothermally treated slag possesses a high mechanical property.[2,7] In addition, it is expected to possess a strong affinity with water owing to the productive phases of hydrate/hydroxide. To introduce the porosity in the resulting solid, the present work attempted to combine slag particles by reactive sintering at the contact points of particles under the hydrothermal condition without densification. The preparation of porous ceramics was carried out by the hydrothermal treatment of BF slag particles and its water retentive property was investigated.

2. Experimental

2.1. Hydrothermal Treatment of BF Slag

The composition of water-cooled BF slag used is summarized in **Table 1**. The slag was granulated to a predetermined size. 1 g of slag particles was mixed with 0.1–0.3 mL of water or 0.05–0.5 M NaOH aqueous solution, and charged in a Teflon crucible (I.D. 12 mm, H 15 mm), which has a 1 mm hole at its lid. The crucible together with 2.5 mL of purified water was placed in a Teflon container (I.D. 26 mm, H 40 mm) of the autoclave as shown in **Fig. 1**. The autoclave was heated to 250°C for 16 h. After cooling to room temperature, the sample was dried in an oven at 80°C for 30 min.

Table 1. Chemical composition of water-cooled BF slag (mass%).

CaO	SiO_2	Al_2O_3	MgO	MnO	T.Fe	S
41.5	35.8	15.3	5.48	0.28	1.58	0.79

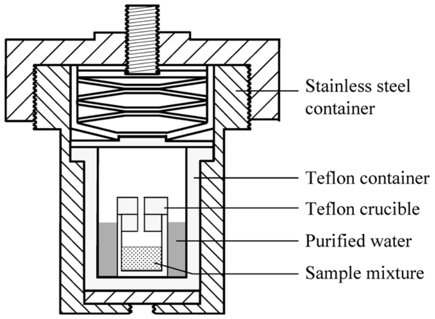

Fig. 1. Schematic diagram of the autoclave used for the hydrothermal treatment of BF slag.

2.2. Water Retention Test of Slag Compact

Slag particles sieved to the predetermined size was added with 10 mass% of 0.1 M NaOH solution and charged in a Teflon crucible of 20 mm diameter. The slag was hydrothermally treated at 250°C for 16 h. The heights of obtained compacts were almost 20 mm. Each compact was dried at 80°C for 2 h, and its volume density was determined by measuring its shape.

The slag compact was immersed in water, and the stored water content was measured from the weight change. The sample after storing water was placed in a constant temperature and humidity chamber, and held at 40% RH and 60°C for 10 h. The temperature of the compact was measured 5 mm below its surface, and the cooling effect is discussed in this paper.

3. Results and Discussion

3.1. Hydrothermal Solidification of Slag Particles

The solidification behavior of BF slag particles after the hydrothermal treatment is summarized in **Table 2**. In the table, a circle denotes solidification to a cylindrical shape, a triangle denotes agglomeration and partial solidification, and a cross denotes the particles remained. Slag did not solidify when mixed with pure water. All slag particles smaller than 125 μm solidified, and compacts were obtained. Solidification became more difficult by increasing the size of the slag particles, and solidification of slag particles larger than 500 μm was strongly affected by the condition of NaOH solution addition. When a solution of 0.1 mL was added, solidification was achieved with a smaller NaOH concentration. Complete solidification was not obtained with 0.3 mL addition. Hence, it was clarified that al-

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Table 2. Tendency for hydrothermal solidification of slag particles after hydrothermal treatment with different NaOH aqueous solution and for different initial particle sizes.

Amount of aqueous solution (ml)	Molarity of NaOH in aqueous solution (M)	Slag particle size (μm)		
		105 ~ 250	250 ~ 500	500 ~
0.1	0 (water)	×	–	–
0.3	0 (water)	×	–	–
0.1	0.05	○	○	○
	0.1	○	○	○
	0.2	○	○	△
	0.3	○	○	×
	0.5	○	△	×
0.3	0.05	○	○	×
	0.1	○	○	△
	0.2	○	○	×
	0.3	○	○	×
	0.5	○	△	×

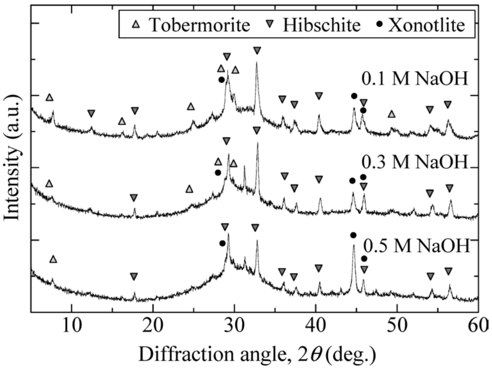

Fig. 2. X-ray diffraction patterns for the slags hydrothermally treated at 250°C for 16 h with the addition of 0.1 mL NaOH solution; initial particle size of 105 to 250 μm.

though the addition of NaOH solution to the slag is effective for its solidification, excess addition results in less solidification. Here, the appropriate addition of NaOH solution for the solidification of BF slag was determined to be 10 mass% at a concentration of 0.1 M NaOH.

Figure 2 shows X-ray diffraction patterns for hydrothermally treated slags with an initial particle size of 105 to 250 μm and the addition of 0.1 mL NaOH solution. The starting material of the slag was almost glassy. Formation of hibschite was observed in slag sample after the hydrothermal treatment, same as in the previous work.[2,6,7] Although tobermorite was also found in the sample with 0.1 M NaOH solution, its formation was suppressed and that of xonotlite increased by increasing NaOH concentration in the solution. Compared with our previous research where hibschite was only formed phase after the hydrothermal treatment of BF slag, it was supposed that further formation of hibschite by NaOH addition decreased the Al_2O_3 content of matrix composition of the slag, leading to the formation of calcium silicate compounds of tobermorite and xonotlite. Tobermorite is known to be the binder phase in the product after the hydrothermal treatment of the $CaO–SiO_2$ system, and the excess addition of NaOH caused less compact solidification.

The typical microstructure of the slag compact is shown in **Fig. 3**. Slag particles contacted each other locally, and an open pore was successfully introduced into the obtained compact. The contact points of the particles are considered to connect mostly with the glass-like phase. To determine the connecting phase, a cross section of the connection area was observed by scanning electron microscopy linked with energy dispersive x-ray analysis and is shown in **Fig. 4**. The structure is mainly composed of three phases: the original slag phase A, needle-shaped crystals B existing between slag particles, and a layered phase C formed on the slag surface that combines two slag particles. The needle-shaped phase was identified as tobermorite from the mass ratio of the components. Since the layered phase at the surface of slag particles was speculated to be the hydrated glass formed after water dissolution into original glass phase in our previous work,[6,7] the glass-like phase connecting slag particles observed in Fig. 3 would be the hydrated glass. Magnesium was concentrated at the hydrated glass compared with the internal unreacted slag phase whereas aluminum and silicon were diluted. Sodium was only detected in the hydrated glass phase in the sample. A portion of the "connecting" hydrated glass is covered with tobermorite crystals as shown in **Fig. 5**. As the tobermorite crystals are considered to give higher joint strength, formation of tobermorite is of importance to the physical property of the porous matrix. NaOH promotes slag solidification by increasing the solubility of silicate ions in the solution leading to crystal formation as well as the faster formation of the hydrated glass layer at the slag surface in view of its existence in the layer. On the other hand, sphere-shaped hibschite crystals surround the surface of slag particles and mostly were not observed at the contacting points, which indicates the less contribution of hibschite for the slag solidification.

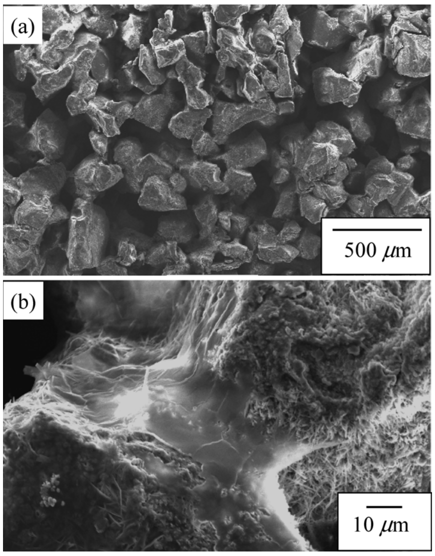

Fig. 3. Microstructure of BF slag compact prepared after hydrothermal treatment at 250°C for 16 h with the addition of 0.1 mL of 0.1 M NaOH solution; initial particle size of 105 to 250 μm. (a) Macroscopic image, (b) detail of the contact point.

3.2. Water Retention of the Slag Compact

The measured volume density and stored water content of slag compacts with different initial particle sizes are summarized in **Table 3**. As the densification progressed with smaller sized slag particles after the hydrothermal re-

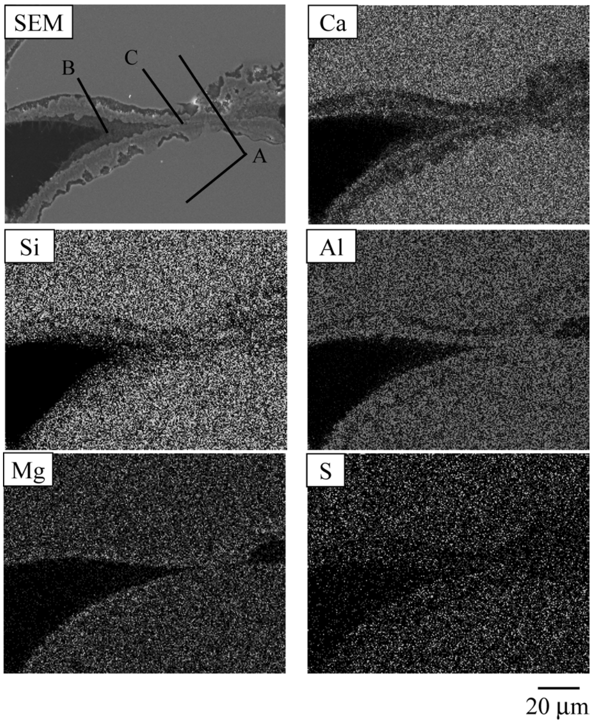

Fig. 4. Cross section of contacting points of slag particles after hydrothermal treatment at 250°C for 16 h with the addition of 0.1 mL of 0.1 M NaOH solution; initial particle size of 105 to 250 µm.

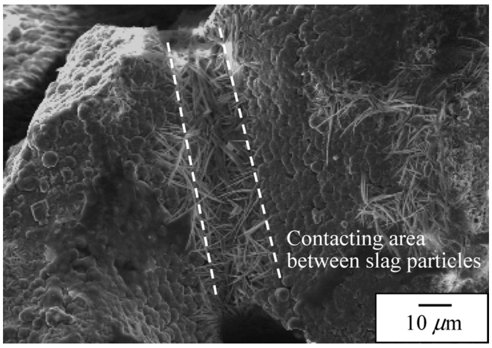

Fig. 5. Typical image of the contact point of slag particles covered with tobermorite crystals; the sample was prepared by hydrothermal treatment of the BF slag particles of 105 to 250 µm at 250°C for 16 h with the addition of 0.1 mL of 0.1 M NaOH solution.

Table 3. Properties of the prepared compacts after the hydrothermal treatment of BF slag particles at 250°C for 16 h.

Initial particle size (µm)	Properties of the prepared compact	
	Volume density (g/cm^3)	Stored water content (vol%)
105~250	1.57	41
250~500	1.35	47
500~	1.45	46

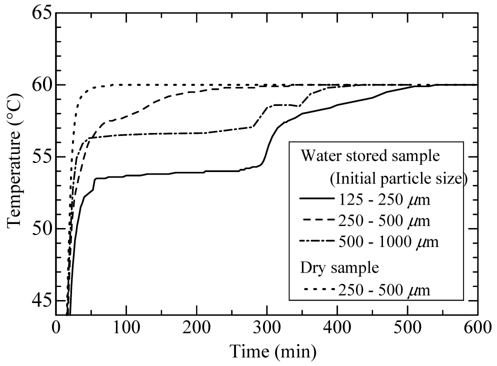

Fig. 6. Heating curves of the BF slag compacts after hydrothermal treatment at 250°C for 16 h with the addition of 0.1 mL of 0.1 M NaOH solution.

action, the stored water content, which was determined as a volume fraction, decreased and the volume density increased.

The slag compacts in Table 3 were subjected to the water retention test. Changes in the sample temperature during the test are shown in **Fig. 6**. After holding for 10 h, water introduced in the compact completely vaporized out. The sample without added water was heated to a surrounding temperature of 60°C within 60 min. On the other hand, the internal temperatures of the water-introduced samples were kept 5–6°C below the surrounding temperature for 5–7 h before they increased gradually. Since it takes 7–10 h to attain to 60°C, a temperature reduction was achieved during the period. By increasing the initial particle size of the BF slag, the cooling effect was suppressed. This might be caused by the smaller heat transfer in the compact with the smaller particle size, which is expected from the large heat resistance with the gas/solid interface. Therefore, it is possible that hydrothermally treated slag can be used as a water retention material owing to its large porosity caused by local binding between slag particles.

4. Conclusions

The preparation of porous ceramics was demonstrated by the hydrothermal treatment of BF slag particles with the addition of NaOH solution at 250°C. In the obtained compact, the particles combined locally at contact points with the hydrothermally reacted phase of hydrated glass and tobermorite. Prepared porous ceramics had a cooling effect during a water retention test and may possibly be used as water-retentive materials.

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