Behavior of Crystallization on a Continuous Solidification Process of Blast Furnace Slag

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A continuous blast furnace slag solidification process was developed to promote the use of air-cooled slag coarse aggregate for concrete. In this process, molten slag can be solidified in only 120 seconds, and the thickness of the slag is about 25 mm. After crushing the slag, the water absorption ratio is much lower than that achieved in the past because gas generation is suppressed. With this apparatus, most of the slag is crystalline, but part of the slag has a glassy surface. Therefore, EPMA and XRD were used to study the glass transition phenomenon. It was found that the thickness of the glass layer is about 2 mm. To discuss the glass transition and crystallization phenomena, the thermal history was simulated by heat transfer analysis. The results clarified the fact that all the slag on the mold has a glassy surface layer of about 2 mm, and good agreement between the calculation and experimental data concerning the layer was obtained. It was also shown that most of the slag crystallizes in the slag pit because the temperature inside the piled slags rises to more than 1 173 K. The measured slag temperature and calculated temperature were also in good agreement.

KEY WORDS: blast furnace slag; air-cooled slag; coarse aggregate; low absorption; crystallization.

1. Introduction

Because air cooled blast furnace slag is porous and has high water absorption in the range of 2.7–5.4%, it is not widely used as coarse aggregate for concrete in Japan.1,2) In order to produce air cooled blast furnace slag with low water absorption similar to that of natural stone, the authors developed a continuous blast furnace slag solidification process.3,4) This process comprises processes in which molten blast furnace slag is poured into molds to a thickness of 20–30 mm, solidified into plates in a short time of about 2 min, and then dropped from the molds into a slag pit and air cooled. This process makes it possible to suppress the formation reactions of gases such as sulfur, nitrogen, etc. that cause pores and pore growth in the slag. Therefore, if the solidified slag plates are crushed to the size of coarse aggregate for concrete, the water absorption of the crushed product can be reduced to 1% or less, which is similar to that of natural stone.

Although most of the plate-shaped solidified slag produced by this process crystallizes, a glassy part remains on the surface of some of the solidified slag plates. If slag with this remaining glass phase is used as coarse aggregate for concrete, adhesion with the cement paste will be poor due to the smooth surface of the coarse aggregate, and the strength of the concrete may possibly decrease.5)

Various analyses of the vitrification and crystallization behaviors of blast furnace slag have been carried out. For example, observation of the crystallization temperature, crystal phase and crystal shape when various additives were added to blast furnace slag was performed by differential thermal analysis, and a kinetic analysis of crystal growth was conducted.6–9) The activation energy of crystallization of glass was also analyzed by differential scanning calorimetry.10–13) The hot thermocouple method is a method for evaluating the crystallization region, and TTT (Time Temperature Transformation) and CCT (Continuous Cooling Transformation) diagrams have been prepared using actual slags for the purpose of effectively utilizing the sensible heat and latent heat of blast furnace slag.14,15) However, these were studies of crystallization behavior under conditions of cooling at a constant cooling rate or temperature holding, and did not investigate the behavior of the glass phase when reheated.

In the continuous blast furnace slag solidification process, it is thought that the glassy part of the surface layer of the solidified slag in the slag pit crystallizes due to the temperature increase resulting from the transfer of heat from the interior of the slag itself. Therefore, in this study, the crystallization behavior of blast furnace slag due to heating after cooling was examined. In addition, necessary high temperature physical properties were measured and a heat transfer analysis was performed in order to clarify the relationship between the thermal history of the slag and vitrification.
2. Experimental Method

2.1. Production Method and Evaluation Method of Plate-Shaped Solidified Slag and Coarse Aggregate

Base on the solidification conditions for reducing the porosity of blast furnace slag reported by Tobo et al., a continuous blast furnace slag solidification facility was constructed. Figure 1 shows the outline of the equipment, and Table 1 shows the equipment specification. This equipment comprises 50 molds arranged in a circle on a moving platform, a trough for pouring the molten slag into the molds, a slag pit for recovery of the solidified slag and a spray nozzle unit for cooling the molds. The mold platform moves at a speed of 3 min/revolution, and the slag flow rate is 2.0 t/min. The slag is poured so that the solidified thickness will be 20–30 mm. The molten slag is cooled for 2 min on the rotating molds, and the solidified slag drops into the slag pit when the molds are inverted. After inversion, the molds are cooled by spraying water from both sides, and the next molten slag is poured after the mold surface has dried.

Approximately 50 t of molten slag was introduced into the blast furnace slag ladle, and of that amount, 30 t was used in the experiment. The samples were recovered from the slag pit the next day and their solidified thickness were measured.

The temperatures of the slag surface and mold surface were measured by using a radiation thermometer and infrared thermography. The thermal emissivity of slag was assumed to be 0.92, which is the same as that reported by Tobo et al. For the thermal emissivity of the molds, the value of the radiation thermometer was calibrated with the value measured by a contact thermometer, resulting in a value of 1.00.

2.2. Observation of Solidified Slag

The plate-shaped solidified slag in the slag pit could be broadly divided into slag that was completely crystalline (crystalline slag) and slag with a glassy surface layer on the side that was in contact with the mold (slag with glass layer). Samples of both types were collected and cut with a diamond saw. Because the slag with the glass layer was brittle, those samples were embedded in epoxy before cutting.

The cross section of the plate-shaped solidified slag was observed by EPMA, and an X-ray diffraction analysis of the crystalline slag and the slag with the glass layer was performed at the air side, inner part and mold side of the slag.

2.3. Observation of Crystallization Behavior

Because the surface of some of the solidified slag had become glassy, its crystallization behavior was investigated by the hot thermocouple method. An outline of the device is shown in Fig. 2. The hot thermocouple method has functions for temperature detection and filament heating, and enables rapid heating and rapid cooling of samples. In-situ observation of the slag during heating and cooling is possible by using a CMOS camera.

As the experimental method, blast furnace slag was heated to 1 693 K at 30 K/s, held at a constant temperature for 3 min, and then vitrified by cooling at approximately 160 K/s. As Kashiwaya et al. clarified the fact that vitrification of blast furnace slag occurs at a cooling rate of 35 K/s or more, this was considered as a cooling condition. Next, blast furnace slag was heated and held as described above, and then vitrified by cooling to room at 160 K/s. Following this, the glassy slag was heated from room temperature to 973 K at approximately 40 K/s, the heating rate was adjusted so as to obtain temperatures of 1 073, 1 173, 1 273 and 1 373 K at the specified rate, and the temperature and time until crystallization occurred were measured by in-situ observation.

2.4. Measurement of High Temperature Physical Properties of Blast Furnace Slag

Various high temperature properties of the blast furnace slag were measured in order to perform a heat transfer analysis.

Thermal diffusivity \(a\) [m²/s] was measured based on JIS R...
Measurement methods of thermal diffusivity, specific heat capacity, and thermal conductivity for fine ceramics by flash method. The measurement instrument was a LFA501 made by Kyoto Electronics Manufacturing Co., Ltd. The sample dimensions were a diameter of 10 mm and thickness of 2 mm, and dgf (dry graphite film: blackening spray) was coated on the sample surface. Measurements were performed under an air atmosphere at room temperature and at intervals of 100 K under a vacuum atmosphere from 373 K to 1 373 K. Density \( \rho \) [kg/m\(^3\)] was obtained from the measured weight and the shape.

The specific heat capacity \( C_p \) [J/(kg K)] was measured by the DSC method using a SRA 449 manufactured by NETZSCH. The sample was disk-shaped with a diameter of 5 mm and thickness of 1 mm. Measurements were performed at intervals of 100 K from 373 K to 1 373 K with a heating rate of 20 K/min under an Ar atmosphere.

Thermal conductivity \( \lambda \) was calculated by using Eq. (1).

\[
\lambda = C_p \times \alpha \times \rho \quad \text{................................. (1)}
\]

For the heat transfer calculation, in the range of 1 473 K to 1 773 K, the measured value of the heat capacity of blast furnace slag reported by Ogino et al.\(^{16}\) was used as the specific heat capacity, a value approximating a straight line was used for the density, and the value reported by Kang et al.\(^{17}\) was used for thermal conductivity.

3. Experimental Results

3.1. Condition of Experiment

Figure 3 shows the condition of production of plate-shaped solidified slag in the continuous blast furnace slag solidification equipment. Molten slag supplied from the blast furnace slag ladle was spread on the molds of the continuous blast furnace slag solidification device, and a condition in which solidification proceeded could be confirmed. Although the surface of the slag immediately after supply to the molds was in red-hot high temperature condition, the temperature of the slag surface decreased and the surface had turned black just before the molds were inverted after 2 min on the molds.

The plate-shaped solidified slag that dropped from the inverted molds was piled in the slag pit. Figure 4 shows the condition of the plate-shaped solidified slag in the slag pit. When the fracture surface of the slag immediately after dropping was observed, the surface had turned black, but the central part of the cross section was still in a red-hot high temperature condition. This was due to the temperature difference between the interior and surfaces, which occurred because the slag on the molds was cooled from the surfaces in contact with the atmosphere and the mold. By weight ratio, 98.6% of the slag recovered after cooling had crystallized. However, in the case of the plate-shaped solidified slag in the outermost layer of the slag piled in the slag pit, the surface which had been in contact with the mold had undergone vitrification.

3.2. Observation of Plate-Shaped Solidified Slag

An example of the chemical composition of the recovered plate-shaped solidified slag is shown in Table 2. Photographs of the crystalline slag are shown in Fig. 5. The photograph in Fig. 5(a) was taken from the side in contact with the mold, and that in Fig. 5(b) was taken from the air side. Both sides of the slag are crystalline, and fine pores could be seen in the surface on the air side. Photographs of the slag with the glass layer are shown in Fig. 6. The air side (Fig. 6(a)) contains fine pores like those in the crystalline...
slag, but on the side in contact with the mold (Fig. 6(b)), a glassy substance having a thickness of approximately 2 mm had formed.

To confirm the formation of the crystal phase or glass phase in the cross-sectional direction of the plate-shaped solidified slag, powder X-ray diffraction measurements of the air side, center and mold side of the crystalline slag and the slag with the glass layer were performed. The results of the powder X-ray diffraction measurements of the crystalline slag and the slag with the glass layer are shown in Figs. 7 and 8, respectively. In the crystalline slag, the main phase was Akermanite at all positions. In the slag with the glass layer, the main phase was also Akermanite in the air side and in the center. However, the mold side was not crystalline, judged from its external appearance, it was glassy.

Furthermore, an EPMA analysis of the air side, center and mold side of the crystalline slag and the slag with the glass layer was also performed to investigate the size of the crystal grains in the cross-sectional direction of the plate-shaped solidified slag. The results of the EPMA analysis of the cross sections of the crystalline slag and the slag with the glass layer are shown in Figs. 9 and 10, respectively. In Figs. 9 and 10, the crystal grain size was small on the mold side. In the center, horn-shaped crystals with a size of approximately 60 μm were observed. On the air side, the crystal grain size was small, as on the mold side. The Ca concentration was homogeneous on the mold side, but had become heterogeneous in the interior of the slag and on the air side. This is attributed to precipitation of CaS and Gehlenite in the cooling process due to the slow cooling rate. Moreover, a large number of voids had existed on the air side. In addition, there was no difference in the crystal grain size of the crystal slag and the slag with the glass layer.

3.3. Crystallization Behavior of Blast Furnace Slag

Figure 11 shows hot thermocouple in-situ photographs when samples were heated to 1 273 K after vitrification of molten blast furnace slag by rapid cooling from 1 693 K. In the glassy state, it was able to confirm that the sample was transparent. And when the sample began crystallizing, the sample gradually became opaque.

![Fig. 7. X-ray diffraction patterns of crystal slag.](image1)

![Fig. 8. X-ray diffraction patterns of slag with glass layer.](image2)

![Fig. 9. Image analysis of crystal slag cross section by EPMA. (Online version in color.)](image3)
The temperature at which the slag began to become opaque was defined as the crystallization starting temperature. Figure 12 shows the results of the crystallization behavior from after glass formation together with the TTT diagram. Under the conditions of heating-up to 1 373 K and 1 273 K, crystallization began before the temperature became uniform, and crystals precipitated at 1 206 K and 1 234 K, respectively. Crystallization did not occur under the heating-up condition of 1 073 K. The crystallization starting temperature was generally consistent with the TTT diagram prepared by Kashiwaya et al.

3.4. High Temperature Physical Properties of Blast Furnace Slag

The temperature dependence of density $\rho$ is shown in Fig. 13. The density of the slag at room temperature was 2.93 g/cm$^3$. The density at 1 373 K decreased by approximately 3% in comparison with the density of room temperature.

The measured results of thermal diffusivity $\alpha$ are shown in Fig. 14. The thermal diffusivity of blast furnace slag had a value between 50 and 75 m$^2$/s.

The measured results of the specific heat capacity $C_p$ of the blast furnace slag are shown in Fig. 15. The specific heat capacity $C_p$ of the blast furnace slag was the same as that of quartz glass.$^{18}$ The thermal conductivity $\lambda$ obtained from the measured
values of the specific heat at constant pressure, thermal diffusivity and density are shown in Fig. 16. The thermal conductivity of the blast furnace slag had a value in the range of 1.6 to 2.0 W/(m·K) and increased as the temperature rose.

4. Discussion

4.1. Conditions of Heat Transfer Analysis

The crystallization behavior of blast furnace slag in this continuous solidification process is considered to be determined by the temperature history of the slag. Therefore, a heat transfer analysis was conducted to simulate the temperature history.

The calculation model used in the heat transfer analysis is shown in Fig. 17. An approximate 1/4 model of the slag on the mold was used to simplify the calculation. In the cooling process on the molds, casting of slag on molds having a rectangular parallelepiped shape with a length of 1,300 mm, width of 400 mm and thickness of 45 mm was assumed. For the solidified thickness of the slag, the four conditions of 15, 20, 25 and 30 mm were used. Because the slag is broken into smaller pieces with a size of about 400 mm square by the impact of dropping into the slag pit, a rectangular shape of 400 mm × 300 mm was assumed in the slag pit.

The boundary conditions from 0 to 120 s when the slag is loaded on the mold are shown in Fig. 18. Based on the measured values, the initial temperature of the slag $T_{SO}$ was set at 1,653 K and the initial temperature of the mold $T_{MO}$ was set at 373 K. Three boundary conditions were assumed, 1) slag/air contact surface, 2) slag/mold contact surface and 3) mold/air contact surface. For the thermal resistance of the slag/mold interface, the 0.0009 (m$^2$·K)/W used by Tobo et al. and 0.009 and 0.00009 (m$^2$·K)/W were studied. In this analysis, conditions in line with the actual measurements were examined by changing the upward and downward heat transfer coefficients in the range of 0–20 W/(m$^2$·K). Heat flux in the slag/mold interface was assumed to be approximately equal to the heat generated by the chemical reaction during solidification. In this paper, the heat flux was not considered for simplicity.

Fig. 14. Temperature dependence of measured thermal diffusivity of blast furnace slag.

Fig. 15. Temperature dependence of measured specific heat of blast furnace slag.

Fig. 16. Temperature dependence of measured thermal conductivity of blast furnace slag.

Fig. 17. a) Calculation model and b) Cross-sectional diagram at 25 mm slag thickness in continuously blast furnace slag solidification process. (Online version in color.)

Fig. 18. Boundary condition from 0 to 120 s in continuously blast furnace slag solidification process. (Online version in color.)
transfer from the side surfaces was assumed to be negligible.

The calculation model when the slag is transferred from the molds to the slag pit is shown in Fig. 19. Two calculation conditions were assumed, a) slag inside the slag pile and b) slag on the surface of slag pile in the pit. As the solidified thickness of the slag, the four conditions of 15, 20, 25 and 30 mm were examined. The temperature $T_{xK}$ of the piled slag changes depending on the thickness of the solidified slag. Therefore, in the each condition, we calculated and used the each value when the temperature distribution in the cross-sectional direction of the plate-shaped solidified slag has become constant.

As the physical property values of the slag used in the heat transfer calculation, the values measured with slag having a crystallization rate of 100% were used.

4.2. Temperature Distributions of Slag on Mold and Mold

Figure 20 shows the measured values and change over time in the calculated values of the air side slag temperature (1) in Fig. 18) when the solidified thickness of the slag was 25 mm. When the initial temperature in the calculation was 1,653 K, the temperature of the slag decreased gradually and reached 1,150 K after 120 s. This was basically in agreement with the measured value. The heat transfer coefficients between the air and the mold and between the air and the slag are 10 W/(m$^2$K).

Next, Fig. 21 shows the change in the mold surface temperature (3) in Fig. 18). When the thermal resistance was 0.0009 (m$^2$K)/W, the calculated value of the mold surface temperature agree well the measured value. Accordingly, 0.0009 (m$^2$K)/W was considered to be an appropriate value for the thermal resistance between the slag and the mold. This value was used in the subsequent heat transfer calculations.

Next, Fig. 22 shows the calculated results for the temperature distributions in the mold and in the slag at 60, 90 and 120 s. Here, −45 to 0 mm on the y-axis is the thickness of the mold, and 0 to 25 mm is the thickness of the slag. At 120 s, the temperature in the center of the slag was 1,505 K, whereas the solidus line of blast furnace slag estimated based on the report by Ogino et al.\(^{16}\) was approximately 1,500 K. From this, it was estimated that the slag center was in an unsolidified state. The temperature on the air side of the slag was 1,150 K, and that on the mold side of the slag was 714 K.

Figure 23 shows the thermal history at various points in the slag (0, 1, 2, 2.5, 3, 5, 25 mm) at times from 0 to 100 s for the slag thickness of 25 mm. Here, 0 mm indicates the temperature at the surface in contact with the mold, and 25 mm indicates the temperature at the surface in contact with the air. The CCT diagram of blast furnace slag measured by Kashiwaya et al.\(^{14}\) is also shown. The positions 0 to 2.5 mm from the mold contact surface were in the range of the cooling rates where vitrification occurs. The thickness of the glassy portion of the recovered slag with the glass layer is
approximately 2 mm, and thus the calculated values agree well the measured values.

4.3. Heat Transfer Analysis of Slag in Slag Pit

Figures 24 and 25 show the thermal histories of the slag arranged on the surface and in the interior of the slag pile at the 0, 1, 2 and 2.5 mm positions in the 25 mm thickness of the solidified slag. From the report by Kashiwaya et al., the crystallization temperature of blast furnace slag is 1 173 K. The temperature of the slag on the surface of the slag pile declined after 190 s without rising to the crystallization temperature. On the other hand, the temperature of slag inside the slag pile rose, exceeded the crystallization temperature after an elapsed time of 150 s, and then became substantially constant at 300 s. Figure 26 shows the temperature distributions in the cross section of the plate-shaped solidified slag at 120 s and 300 s in the 25 mm thickness of the solidified slag. It was found that the temperature inside the slag became almost constant at 1 300 K at 300 s, that is, 120 s after the slag was dropped into the pit. This uniform temperature distribution is explained by the fact that the heat in the interior of the slag is transferred to the slag surface after the slag is dropped into the pit at 120 s, and the temperatures of the mold side and air side of the slag increase due to the heat of the piled slag surrounding the slag. Next, Fig. 27 shows the relationship between the temperature of the mold side of the plate-shaped solidified slag that exists inside the piled slag and the solidified thickness of the slag. When the slag was dropped from the mold into the pit at 120 s, the calculated values of the mold side temperature are approximately 700 K regardless of the solidified thickness of the slag. The calculated value of the mold side temperature at 300 s showed a correlation with the solidified thickness, and exceeded the crystallization temperature when the solidified thickness exceeded 20 mm. Figure 27 shows the measured value of the temperature inside the piled layer in the pit measured by infrared thermography. These are the measured values of 11 experiments. The solidified thickness at each point is the average value of the plate-shaped solidified slag recovered after cooling. The measured temperatures are in good agreement with the calculated temperature at 300 s. As the solidified thickness becomes thinner, the sensible heat held by the entire piece of slag decreases. Therefore, it is thought that the heating value transferred from the slag to the mold during the period 0–120 s, when the slag is on
the mold, has a larger influence on the decrease in the slag temperature when the slag thickness is thinner.

Accordingly, although vitrification of the slag on the mold occurs in the region from the mold side of the slag to a depth of 2 mm, if the solidified thickness is 20 mm or more, the temperature will increase due to piling in the slag pit, and this vitrified part will undergo crystallization. However, since some of the plate-shaped solidified slag is cooled at the outer surface of the slag pile, the glass layer of these slags will remain in the vitrified state. The ratio of the remaining glass phase in coarse aggregate produced by crushing/size adjustment of plate-shaped solidified slag with an average solidified thickness of approximately 25 mm was 1.4%. The compressive strength of concrete prepared by mixing this coarse aggregate was similar to that of concrete made with natural stone.

5. Conclusion

The following knowledge concerning the crystallization behavior of slag in the continuous blast furnace slag solidification process were obtained.

(1) Two types of slag are obtained in this process; the larger part is crystallized slag which is held in the interior of the slag pit, and the remainder is slag with a 2 mm thick vitrified surface layer.

(2) According to a heat transfer analysis, approximately 2 mm of the plate-shaped solidified slag which is in contact with the mold undergoes vitrification. That result is approximately in agreement with the measured glass thickness. Subsequently, the temperature in the thickness direction of the plate-shaped solidified slag becomes almost constant as a result of holding in the piled layer of plate-shaped solidified slag. If the solidified thickness of the slag is 20 mm or more, the entire slag will reach a temperature exceeding the crystallization temperature due to holding in the piled layer, and the vitrified part will undergo crystallization.

(3) In the plate-shaped solidified slag at the surface layer of the slag pile, the temperature of the side in contact with the air will not exceed the crystallization temperature, and as a result, the vitrified part will remain. However, the ratio of the remaining glass phase in coarse aggregate produced by crushing/size adjustment of plate-shaped solidified slag with an average solidified thickness of approximately 25 mm was 1.4%.

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