Characteristics of Glass Beads from Molten Slag Produced by Rotary Cup Atomizer

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Steelmaking is well known to be one of the highest energy-consuming industries, where high temperature molten slag is discharged without any heat recovery. This paper describes the hot experiments where a Rotary Cup Atomizer (RCA) is used to produce dry glassy slag without water impingement. In this, the properties for granulated slag were chiefly investigated. Molten slag was first poured onto the center of the rotating cup at various rotating speeds. Slag granulation was then observed using a video camera, and finally, the particles were collected for physical and chemical analyses. The results of XRD and DSC analyses demonstrate that all slag drops obtained by the RCA method are undoubtedly glassy. The particle size of the granulated slag is strongly controlled by both the diameter of the cup and the speed of rotation. The relationship between the particle size and the two parameters is expressed as $D_p = 16.86/r_{o}$, Smaller particles that produced at a higher rotating speed seem to be more transparent or glassy and have compression strength twice higher in comparison with water granulated slag. The data obtained will provide valuable information not only for producing glassy slag, but also for exchanging energy between gas and molten slag efficiently.

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1. Introduction

As steel consumption increases, pig iron production also increases, thus causing an increase in the consumption of raw materials such as iron ore, scrap, flux as well as fuel or energy. Such a process discharges a certain amount of slag and exhaust gas as well as heat from both of them. In Japan, the steel industry produces approximately 37.6 Mt of slag per year and most of them is discharged from blast furnace. The molten slag has been treated by conventional water-cooling method without any recovery of heat in spite of its big potential. Therefore, large amounts of heat, including that from the molten slag is wasted and this is drawing attention from both the environmental and the energy aspects. Besides that, the blast furnace slag must have certain properties in order to be used in the production of Portland cement.

In conventional process, molten slag is quenched rapidly using a large amount of water to produce a glassy-granulated slag. The product is then dried before it is used for raw materials of roadbed or cement production. However, this process causes in environmental problems such, water pollution caused by alkaline elements in the slag, air pollution caused by sulfide gas. Also, extra energy for drying as well as too much water is necessary to granulate the slag at high temperature. For the water-cooling process, approximately US$10 is spent per each ton of molten slag. Recently, dry granulation using Rotary Cup Atomizer has been proposed to solve the problems. The process is first introduced by Pickering et al. to granulate molten blast furnace slag under air blasting, combined with steam and hot water production using heat from the slag. Feasibility of the process has been reported in the previous study. However, there is lack of information regarding the properties of the granulated slag produced. Therefore, the purpose of this work is to clarify the characteristics of the granulated slag from rotary cup atomizer in order to advance-used of the slag product.

2. Experimental

Figure 1 shows a schematic diagram of the RCA equipment used in this experiment. It mainly consists of four parts: (1) A slag feeder having a hole at the bottom and a graphite stick as a stopper; (2) Rotary cup having 140 mm in diameter and 30 mm in thick, is driven by a motor and has a maximum rotating speed of $83.3 \text{s}^{-1}$; (3) Particle collector, a sheet for collecting the slag drops; (4) Monitoring equipment, a video camera connected to a monitor that is placed on the cover of RCA for direct observation. The cup is set after embedding fire-resistant cement in a stainless steel plate. A molten blast furnace slag, taken from JFE Steel, Chiba Factory, and having a temperature of over 1723 K was employed in this experiment. The major chemical compositions of slag are 33.7 mass% of SiO$_2$, 15.0 mass% of Al$_2$O$_3$, 42.2 mass% of...
CaO, and 6.6 mass% of MgO.

For each experiment, 3 kg of slag was melted in a high induction furnace and kept at a temperature of approximately 1723 K. This experiment was carried out in atmosphere condition. The cup of the RCA was preheated using a gas burner in order to avoid breakage due to thermal shock before pouring the molten slag. The slag temperature was measured by a thermocouple, which was inserted into the molten slag in the induction furnace. After reaching the desired the rotation speed, the molten slag was poured from the feeder on the top into the center of the cup. A thin film of slag was spanned out and extended radially from the lip of the cup and then broke up on its own accord. During atomization, the mechanism of slag granulation was simultaneously observed by a video camera. The slag drops were collected and then classified based on their shape and dimension using a sieve. The weight of the slag was also measured according to the different particle size.

Differential scanning calorimetry (DSC) measurement was performed under argon gas flow at 10 K/min of heating rate followed by cooling down after holding for 15 min at desired temperature. X-ray diffraction (XRD) was used to investigate the crystalline of the slag corresponding to the DSC patterns. The strength of the slag was measured using a hydraulic compression machine and the results were compared with water-granulated slag. The analyses of sample were conducted after dried to release moisture. However, the crushing test for dry granulated slag using RCA was carried out without any treatment before.

3. Results and Discussion

3.1 Characteristics of dispersion patterns of molten slag on the cup surface

Figures 2(a) and (b) show the appearances of molten slag at different rotating speed. At 16.6 s⁻¹ as shown in (a), a part of the slag is dispersed over the center of the cup. (b) shows that the molten slag is completely dispersed from the whole edge of the lip of the cup and the dispersion seems to be in a smooth line. By increasing the rotating speed to 33.3 s⁻¹, the slag is dispersed from the whole cup surface without any interference and, it stopped overcoming the cup. A fine dispersion of slag is clearly shown in (b) in which the molten slag is dispersed smoothly from the center of the cup. At a low rotating speed, as show in (a), the centrifugal force that occurred from these conditions is not strong enough to disperse the molten slag at the center of the cup surface since its gravitational force is relatively larger than the centrifugal force. In this condition relatively coarse particle dispersion is occurred. These results show that the dispersion of slag on the cup is strongly controlled by the centrifugal force, which increases with high rotating speeds, and avoids dispersion over the cup.

3.2 Particle size distribution of granulated slag

Table 1 gives the weight of granulated slag collected under different experimental conditions. More than 80 mass% (approximately 2.4 kg of a 3 kg sample) of granulated slag was collected for all the experiments, and the other 20 mass% of the slag was adhered to the cover or remained in the cup. We should note that the collected granulated slag is divided into two parts; the inside and the outside of the collector box. The slag outside the collector box refers to the slag, which adhered to the wall of the RCA cover. About 17% of the total amount of slag collected is obtained from the collector sheet. The slag collected from both the inside and outside of the collector box is separated from the spherical and non-spherical particles. Particles collected from outside the collector box have a small spherical form since the other part is mostly flushed and stuck with each other on the wall of the RCA cover. The weight of the spherical particle inside the collector box varies with the rotating speed. About 31 mass% of the spherical particles are obtained at 16.6 s⁻¹. The numbers of the particles increase at higher rotating speed of.

<table>
<thead>
<tr>
<th>Rotating speed (s⁻¹)</th>
<th>Inside collector</th>
<th>Outside collector</th>
<th>Total weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside sum (g)</td>
<td>Granulated particles (g)</td>
<td>Inside sum (g)</td>
<td>Granulated particles (g)</td>
</tr>
<tr>
<td>16.6</td>
<td>382.5</td>
<td>117.5 (31%)</td>
<td>2141.3</td>
</tr>
<tr>
<td>33.3</td>
<td>427.5</td>
<td>357.6 (84%)</td>
<td>2067.6</td>
</tr>
<tr>
<td>50</td>
<td>431.9</td>
<td>406.9 (94%)</td>
<td>2008.5</td>
</tr>
<tr>
<td>Average</td>
<td>414 (17%)</td>
<td>2072 (83%)</td>
<td>2486</td>
</tr>
</tbody>
</table>

Table 1 Weight of granulated slag collected in each experimental condition

Fig. 2 Appearances of slag dispersion using wheel type of cup.
84 and 94 mass% for 33.3 and 50 s\(^{-1}\), respectively. The largest numbers of particles are obtained when the small particles are produced. The reason is that increasing the rotating speed resulted in high centrifugal force, and this produces smooth dispersion with small particles. The production of small particle by increasing the cooling speed due to high specific surface area promotes the granulation process easily by preventing from the adherence of slag.

Figure 3 shows the measured diameter of the slag drops. As it is considered, the particle diameter obtained from this experiment is strongly controlled by rotating speed. The figure shows that the diameter of the granulated slag decreases sharply at a lower zone of rotating speed and diameter decrease becomes smaller above the initial rotating speed of over 10 s\(^{-1}\). To simplify the data analyses, the tangential velocity is obtained by multiplying the rotating speed and the cup diameter (\(\omega r \))

\[
D_p = \frac{16.86}{\omega r}
\]

where, \(D_p\) is the particle diameter (mm), \(r\) is radius of cup (mm) and \(\omega\) is the tangential velocity. The particles have a similar average diameter when the peripheral velocity is the same, regardless of whether the cup diameter is changed or not. Increasing the peripheral velocity decreases the particle diameter and the change in ratio decreases at a high velocity.

In order to verify the validity of the data obtained in these experiments, an empirical equation proposed by Frazer \textit{et al.} was used in this evaluation. Originally, this equation was given with a non-SI unit and usually compatible to predict the drop diameter of a flat disk. The calculated data by Frazer’s equation was expressed as solid line in Fig. 3. The deviation between the measured and the calculated data at a low rotating speed is probably because of the dispersion of slag. The results suggest that a higher rotating speed provides a better condition to produce a fine particle for in which rotating speed is one of the key operating parameters to control particle size.

### 3.3 Characteristics of granulate slag

Figures 4(a)–(b) show the appearances of RCA-granulated slag, compared with water-granulated slag (c). (a) and (b) correspond to 16.6 and 50 s\(^{-1}\), respectively. Both of the RCA-granulated slags produced are in the shape of spherical. The diameters for the granulated slag obtained at 16.6 s\(^{-1}\) vary from 0.5 to 5.0 mm where large particles are dominant among them and the appearance of drops are rather cloudy. In contrast, the granulated slag drops at 50 s\(^{-1}\) are uniformly spherical with diameter less than 1 mm and transparent or like glass. Accordingly, a high rotating speed promotes in fine particle and fastening the cooling process due to large surface area. The water-granulated slag is flake like shape. Its size distribution is widely diverse from the fine to coarse particle. Therefore, it needs further mechanical or grinding process to make near spherical before utilizing the slag. However, RCA of molten slag does not need such extra processes.

Figure 5 shows prediction of temperature changes during cooling of the RCA-granulated slags. The temperature changes was calculated for a single particle with diameter of 2.5 mm based on the heat transfer analysis method for a spherical single particle proposed by Akiyama. Analysis was conducted with assumptions that; the molten slag was completely granulated; the temperature inside the slag is uniform, as an initial condition and heat conduction occurs concentrically. The result indicates that the maximum temperature difference between the center and at the surface of the particle was 122 K. The inside temperature of the particle decreases from the center to the surface, indicating that cooling rate in center is lower than the surface.
possible that the particle adheres to the wall surface if it cools slowly. According to the experiment, the time required for the particle to drop onto the collector surface was approximately 0.5 s. The time required for cooling the slag is longer than that for dropping. These phenomena suggest the possibility of adhering/sticking with the collector of slag and cause a low glass conversion ratio of granulated slag with a big size.

Figure 6 shows the DSC curves of the three samples obtained under the nitrogen atmosphere. Three kinds of sample are used for the analysis: air cooling slag; RCA slag (obtained using a RCA that has a diameter of about 0.6 mm); water cooling slag. Three points appear in the curves, indicating the properties of glass, the deviation curve starts at about 600 K, peaks about 1200 K and reversible peaks occur over 1400 K. The first deviation or the intersection of the straight lines extending from the tangents of the DSC, in the region of the baseline shift, indicates the glass transition temperature. The exothermic peaks appear at about 1200 K, indicating the crystallization of glass. The last endothermic peak about 1400 K should be involved in the melting of some crystalline phases. Attention is focused on the crystallization area. There is a very small or nearly a disappearing peak for an air-cooled slag at the crystallization temperature. It indicates that the air cooling process does not result in glassy slag. However, the peaks indicating the crystallization of glass appeared in the RCA slag and the water-cooled one. Both the slag crystallized in this manner has similar peaks with the same exothermic heat of 170 kJ·kg⁻¹ approximately. Davies reported that the difference in the pretreatment of the slag resulted in the differences in the endothermic and exothermic points since they related to the nucleation and crystallization processes. Also, the difference in the particle size may also be affected with that of the peak’s maxima, as shown in Fig. 6, that has no effect on the glass transition temperature. Figure 7 shows XRD patterns of the two samples: RCA and water-granulated slags. Both of the granulated slags are similar, indicating glassy structure. Similar feature is also reported by Fredericci. The exothermic peak observed in the DSC pattern of glassy slag is associated with the crystallization of a meta-stable phase. Since the major constituents of the glassy slag are CaO, SiO₂, Al₂O₃ and MgO, the meta-stable phase in the present result should be a compound composed of the four constituents listed above. Williamson and Rogers revealed that the main crystalline phases are solid solutions of 2CaO·Al₂O₃·SiO₂ and 2CaO·MgO·2SiO₂ and such a series is popularly known as the melilite series in which their crystallizations and growth are affected by the addition of a small amount of iron oxide by making a spinel. The melilite peaks are obtained for the sample prepared by air cooling as shown in Fig. 7. They did not appear in the glassy slags from both RCA and water cooling. As a result, the glassy ratio of the slag granulated using RCA is present in the same as the water granulated one as revealed by the similarity in their intensities. Therefore, although RCA process is conducted in air condition, the difference in cooling speed is not significant in comparison with the water-cooling process due to the large specific surface area of the small particle produced using a RCA.

Granulation using RCA resulted in a relatively high strength material comparing with water granulation method. Figure 8 shows the compression strength of the original RCA slag and after heat treatment. A single particle of the RCA slag with diameter of 2 mm has compression strength about...
This strength is twice higher than that of slag produced by water granulation. It can be explained that the appearance of three kinds slag in Fig. 4, the RCA slag seem more compact and spherical solid, compared with porous and irregular particles for water-granulated slag. Therefore the granulation resulted from RCA makes the slag strong, even if the process is conducted in dry condition without any water impinging. The RCA slag was heated up at highest temperature of 1473 K and holding time for 15 min then cooling down slowly to atmosphere. The strength of heated slag dropped at about half from the original. Rapid cooling during atomization prevents from the crystal nucleation and growth, and results in the glass structure keeping high energy. Heating up the glassy slag above 1000 K breaks the glass transition zone as shown in DSC curves. The high energy kept in the glass structure is released as temperature increases. Slow cooling of the slag promotes the recrystallization and crystal growth that make the slag weak.

Recently, attention is focused on the processing of molten slag and recovering of its the sensible heat during the granulation process. An impingement of mixed methane and steam water would rapidly speed-up the nucleation and crystallization growth of the glass slag. According to the previous results, the impinging of gas or air promotes the production of a smaller size granulated slag. Therefore, the mixed methane and steam water would act as a cooling media to produce a fine granulated slag. The fine granulated slag is expected to promote the rate of the methane-steam reforming reaction to produce hydrogen as a final product. The data obtained in this experiment is expected to be useful information for exchanging energy in the gas and molten slag efficiently. If the proposed process is operated well industrially, then it will solve an environmental problem in the steel industry and the fine glassy granulated slag produced will be a useful material for efficient production of cement.

4. Conclusions

The fine glassy granulated slag was prepared from molten blast furnace slag by the Rotary Cup Atomizer method (RCA) without any water-quenched or air-blasting. High rotating speed results in fine homogeneous spherical form. The compression strength of the slag particles by RCA is twice higher that of the water-granulated one. Therefore, RCA is expected to be a useful method for efficient cement production.

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REFERENCES