Effects of 28 GHz/2.45 GHz Microwave Irradiation on the Crystallization of Blast Furnace Slag

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The effects of microwave irradiation on the crystallization of 40%CaO–40%SiO₂–20%Al₂O₃ synthesized slag and actual blast furnace slag were investigated using a 28 GHz multimode microwave irradiation system, a commercial microwave oven (2.45 GHz), and an electric resistance furnace. While it was observed that the 2.45 GHz centimeter-wave had little effect on the samples, the 28 GHz millimeter-wave was found to accelerate crystallization significantly, especially at lower temperatures at which the crystalline phases are never generated by external heating.

Further, the effects of the precipitated phases and impurities on the crystallization with the 28 GHz microwave irradiation were investigated. The temperature of the glassy slag increased more rapidly when compared with the crystalline phases that exist in the actual blast furnace slag. In addition, a small amount of impurity was found to improve the heating property of the slags.

KEY WORDS: blast furnace slag; recycling; crystallization; microwave; millimeter-wave; non-thermal effect.

1. Introduction

In Japan, approximately 25 million tons of blast furnace slag has been generated in the production of approximately 100 million tons of steel every year. Blast furnace slag is classified into water-quenched slag and slowly-cooled slag. Water-quenched slag exists in an almost glassy state and is used as a component of blast furnace cement or as fine aggregates, whereas slowly-cooled slag exists in a well-crystallized state and is used as coarse aggregates or in road beds. Blast furnace slag is conventionally recycled in this manner; however, its additional uses should be researched in order to establish a sustainable society. Physical and chemical properties of slag such as strength, hardness, hydraulic property etc. are considerably influenced by composition, morphology etc. Among them, the degree of crystallization is focused on in this paper.

On the other hand, microwave processing is a fast and efficient technique for heating materials that have high dielectric losses or high electrical conductivities, because these materials can be heated by themselves. We have used this property in various processes such as the heat characterization of CaO–SiO₂–FeO slags,1) resource recovery from steel-making slags2) and refractories.3) Further more, it is known that microwaves also influence diffusion and reactions. These influences are called “non-thermal effects,”4,5) and was found that these effects become more apparent in 28 GHz millimeter-wave irradiation experiments than in the 2.45 GHz centimeter-wave experiment.6,7) These advantages were discovered during the investigation of ceramic sintering and metallurgical processing. However microwave effects on the crystallization of glassy materials has not been sufficiently investigated. If the microwave can accelerate the crystallization of slags, we can find not only an effective heat treatment of slags but also the possibility of a new process for production of crystallized glass.

Based on these matters, 28 GHz/2.45 GHz microwave effects on the crystallization of blast furnace slag were investigated.

2. Experimental

2.1. Preparation of Experimental Materials

Actual blast furnace slag and synthesized slags were used in the experiment. Their compositions are listed in Table 1. The synthesized slags were prepared from reagent grade chemicals such as SiO₂, Al₂O₃, and CaO calcined from CaCO₃. They were well mixed and premelted at 1600°C in a platinum crucible under air and quenched by spreading it on an iron plate. The synthesized slag is almost

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Others</th>
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<tbody>
<tr>
<td>BF Slag</td>
<td>34.5</td>
<td>43.2</td>
<td>14.0</td>
<td>4.47</td>
</tr>
<tr>
<td>Syn. Slag</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>-</td>
</tr>
</tbody>
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glassy and the equilibrium phases for its composition are CaO·SiO2, 2CaO·Al2O3·SiO2, and CaO·Al2O3·2SiO2. Since various impurities excluding CaO, SiO2, and Al2O3 are also present in actual blast furnace slags, FeO, TiO2, and MgO were added to the synthesized slags in order to examine the effect of these impurities. All the samples were then grounded to a powder (74–149 μm) and confirmation analysis was performed by using the SiO2 weight analysis method and ICP-AES.

2.2. Heat Treatment of Slags

Blast furnace slag and synthesized slag were treated with 2.45 GHz/28 GHz microwave irradiation and external heating in an SiC electric resistance furnace. In all experiments, the sample weights were 0.5–1 g.

The experimental apparatus used in the microwave irradiation and external heating are shown in Fig. 1. A 28 GHz, 1.0–3.0 kW multimode microwave (Model FMS-10-28, Fuji Dempa Kogyo Co., Ltd., Japan) was used in the 28 GHz microwave heat treatment. The samples were charged in a quartz tube and their temperatures were measured using a sheathed thermocouple set in the thinner quartz tube. This was followed by microwave irradiation in air. After heating, the samples were cooled in air.

In the 2.45 GHz irradiation experiment, a commercial microwave oven (Sharp Co. Ltd. RE-6200) that can radiate a 2.45 GHz, 1.6 kW multimode microwave was used. SiC granules (5 mm) were used as an auxiliary heat source (hybrid heating) since the samples did not heat up sufficiently to be crystallized by themselves. During the heating, the temperature of the sample was monitored using a dual wavelength pyrometer (CHINO IR-AQ) through a 5 mm diameter hole in the insulation, and controlled by turning the microwave on and off. After irradiation, the samples were removed from the insulation and cooled in air.

In the conventional external heating experiment, an SiC electric resistance furnace was used and the temperature around the sample was monitored by a Pt–Rh thermocouple.

After the heat treatment, all the samples were once again grounded to a powder (~74 μm) and then subjected to XRD analysis. The degree of crystallization was then estimated by the internal standard method using TiO2 as the internal standard and glassy synthesized slag as the matrix.

3. Results and Discussion

The temperature behavior during the external heating experiment and the XRD patterns of the sample maintained at controlled temperatures for 3 min are shown in Fig. 2(c) and Fig. 3(c), respectively. At 900°C, the sample softened during the heating; however, the crystalline phases did not appear within 1 h of heat treatment. Crystalline phases such as CaO·SiO2, 2CaO·Al2O3·SiO2, and CaO·Al2O3·2SiO2 were formed at temperatures above 1 000°C.

The variation of the crystallization fraction with time at 1 000°C was then investigated (Fig. 4). Crystalline phases appeared in the following order: CaO·SiO2, 2CaO·Al2O3·SiO2, and CaO·Al2O3·2SiO2. The total crystallization fraction increased rapidly in the first 30 min.

In the 2.45 GHz centimeter-wave irradiation experiment, the temperatures of the samples fluctuated cyclically due to microwave control (Fig. 2(b)). However, the temperature behavior was almost the same as that in the external heating.
experiment. Figure 3(b) shows the XRD patterns of the samples after 3 min.

During the 28 GHz millimeter-wave irradiation experiment, two typical temperature behaviors were observed, as shown in Fig. 2(a). Some of the curves demonstrated a critical point where the temperature began to increase rapidly. This behavior was not demonstrated in other cases. The sample became clouded and crystalline phases could be detected by XRD only when a rapid temperature increase was observed (Fig 3(a)). This rapid temperature rise can be due to thermal runaway. For the experimental setting and samples used in this study, the sub-threshold power was approximately 1.8 kW. The holding temperature may be determined by a heat balance.

A minor difference was detected between the experimental results of external heating and 2.45 GHz microwave hybrid heating. For example, crystalline phases did not appear at 800°C, and the crystalline phases and crystallization fraction were almost the same at 1 100°C. For the 28 GHz millimeter-wave irradiation experiment, a high crystallization fraction was observed at lower temperatures (800°C), whereas no crystallization was detected for external heating. Moreover, it was found that the degree of crystallization in the sample processed for 3 min by 28 GHz microwave irradiation was equal to that of the sample processed for 20–30 min by external heating. Accordingly, a non-thermal effect of the 28 GHz microwave irradiation, namely the promotion of crystallization, was observed.

From the temperature curves for the 28 GHz microwave treatment, it was predicted that the rapid temperature increase was due to the formation of a specified crystalline phase that efficiently absorbs microwaves. Then, in order to determine the relationship between the critical temperature step and the formation of crystalline phases, CaO·Al₂O₃·2SiO₂, 2CaO·Al₂O₃·SiO₂, and CaO·Al₂O₃·2SiO₂ were treated by 28 GHz millimeter wave irradiation. As a result, the temperature increase in each crystalline phase was slower than that in the glassy synthesized slag (Fig. 5). As mentioned
above, the microwave effect on the crystalline phase is less than that on the glassy phase. Therefore, it is considered that a microscopic non-equilibrium state was achieved; as a result, crystalline phases could be generated even at lower temperatures that were measured by the thermocouple.

The effect of 2 mass% addition of FeO, TiO₂, MgO, or Na₂O was examined. As shown in Fig. 6, the samples were heated easier than pure synthesized slag, even for a comparatively lower microwave power. In particular, when FeO was added, the critical temperature decreased significantly, and crystalline phases were observed by XRD (Fig. 7) in the sample after heating, even though the maximum temperature was as low as 630°C. On the other hand, the crystalline phases were not detected in the same slags treated at 900°C by external heating. From this, the non-thermal effect of the 28 GHz microwave was confirmed. In the experiment, the critical temperature tended to decrease for the actual blast furnace slag; this was considered to be mainly due to the FeO content.

4. Conclusions

The effects of microwave (28 GHz/2.45 GHz) irradiation on the crystallization of the synthesized CaO–SiO₂–Al₂O₃ slags and actual blast furnace slag were investigated. The microwave-irradiated samples were then compared with the samples heated in an electric resistance furnace. The results obtained are summarized as follows:

(1) 28 GHz microwaves were able to crystallize the CaO–SiO₂–Al₂O₃ slag, whereas an auxiliary heat source (SiC granule) was required in the 2.45 GHz microwave irradiation experiment.

(2) While the effect of the 2.45 GHz centimeter wave on the crystallization of the CaO–SiO₂–Al₂O₃ slag was not observed, the 28 GHz millimeter wave was found to accelerate the crystallization, especially at lower temperatures.

(3) In the microwave irradiation of the CaO–SiO₂–Al₂O₃ system slag, the temperature increase in the crystalline phases is slower than that in the glassy phase.

(4) A small amount of impurities caused the acceleration of the heating by microwave irradiation.

REFERENCES