Carbothermic Reduction of MgO by Microwave Irradiation

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A new method has been developed to produce magnesium vapor for deoxidation or desulfurization of molten iron. Microwave heating of magnesium oxide and graphite powder mixtures was carried out in air or argon flowing atmosphere, utilizing a commercial microwave oven operated at 2.45 GHz. Progress of carbothermic reduction of MgO was observed, and the influences of morphology and carbon content of the samples on the heating behavior and the fractional reduction of MgO were investigated. Particularly, the initial graphite particle size was found as an important factor for heating and reduction behavior. Also, MgO–C brick was subjected to the microwave treatment and was found to be a candidate as Mg sources.

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1. Introduction

In recent years, due to growing demands for high quality steels, more effective processes for desulfurization and deoxidation are expected to be developed. Owing to its strong affinity for sulfur and oxygen, attention is paid to magnesium as a desulfurizer or deoxidizer. Several methods have been studied for magnesium desulfurization, such as magnesium injection,1) magnesium wire,2) Mag-Coke,3) Mag-Lime4) addition and CaO-magnesium powder injection.5) In each method, desulfurization efficiency of magnesium was not high enough because large amount of magnesium was lost from the iron due to high vapor pressure of magnesium. Accordingly, it is preferable to add magnesium to molten iron as a vapor phase for effective desulfurization. Irons and Guthrie6) studied the kinetic mechanism of desulfurization of molten iron with magnesium vapor. Shan et al.7) studied desulfurization of molten iron with magnesium vapor produced in-situ by carbothermic reduction of MgO. They produced magnesium vapor by immersing an alumina tube filled with MgO-graphite pellets into molten iron. Yang et al.8) studied deoxidation of molten iron with Mg vapor produced similarly as mentioned above. Such a desulfurization or deoxidation method might be a promising way at low cost. But it is questionable whether the sufficient energy for carbothermic reduction of MgO can be supplied within a few minutes only by external heat transfer in a large scale of a practical steelmaking.

For assisting heat supply to MgO-graphite mixtures, we focussed on microwave heating in the present work. Microwave heating may bring great advantages in such batch processes because it provides internal and rapid heating. There is a great possibility to produce magnesium vapor by microwave irradiation in the immersion tube filled with MgO–C mixtures.

Several studies have been made on microwave synthesis in material processing and metallurgy. Standish et al.9) investigated the carbothermic reduction of iron oxides with microwave heating and obtained higher reduction ratio than resistance heating within the shorter processing time. Kozuka et al.10) reported the influences of powder pressing and carbon content on heating behavior in the microwave synthesis of SiO2/C mixtures. Morita et al. investigated the melting and reduction treatment of slags11,12) and found the relationship between dielectric factor and heating behavior of slags.

In the present work, microwave synthesis was applied to MgO–C system. Heating of the MgO–C mixtures with microwave irradiation was mainly due to Joule heating of graphite particles for lacking in dielectric compounds. Therefore, the influences of morphology and carbon content on the reduction were investigated. Also, in order to evaluate the possibility of the utilization of waste refractories as a Mg source, MgO–C brick was also subjected to microwave irradiation.

2. Experimental

Microwave heating was carried out in a commercial microwave oven (2.45 GHz, 1.6 kW, Sharp Co. Ltd. R6200). A schematic diagram of the experimental apparatus is shown in Fig. 1(a). A weighed MgO and graphite mixture (4 g) was charged in a quartz crucible (25-mm o.d., 21-mm i.d., 50-mm high) for temperature measurements, or in an alumina crucible (38-mm o.d., 32-mm i.d., 50-mm high) for fractional reduction measurements respectively, which was then placed onto an insulating brick located in the center of the oven. Temperature of the sample was measured through a 5 mm diameter hole in the insulation, only when it was higher than 973 K due to the feature of the pyrometer used in this work. After microwave irradiation, the sample was cooled to the room temperature in the oven, then subjected to weighing and the chemical analyses for the reduction ratio measurements. We defined the reduction ratio as the following equation.

\[
\text{Fractional reduction (\%)} = \frac{100(1 - W)}{W_0}
\]

Here, \(W_0\) is an initial MgO weight and \(W\) is a MgO weight after Microwave irradiation.

When the progress of carbothermic reduction of MgO with microwave irradiation was investigated, another alumina
3. Experimental Results and Discussion

3.1 Effect of powder pressing

3.1.1 Heating behavior

Heating behavior of MgO–C mixtures of various carbon amount were shown in Fig. 2(a). Here, the amount of carbon required for the reduction of MgO into pure Mg is defined as carbon equivalent (C_{eq}) in this paper.

\[
C_{eq} = \frac{X_{\text{Graphite}}}{X_{\text{MgO}}} \tag{1}
\]

Here, \(X_{\text{Graphite}}\) and \(X_{\text{MgO}}\) are the initial molar fractions of graphite and MgO in the samples, respectively. The samples of \(C_{eq}\) less than 3 were not heated above 973 K in 480 s. For all other samples, the temperature was raised and leveled off within 200 s. As seen in Fig. 2, the final temperature of the sample of \(C_{eq}\) 3 was the highest, and the heating rate of graphite was the largest. These can be explained quantitatively as follows. Since the MgO–C samples are considered to be heated by the Joule effect of graphite under microwave irradiation, total generated heat increases with increasing carbon equivalent of the samples. On the contrary, due to the large thermal conductivity of carbon, over-all conductivity of the samples increases and heat loss from the mixtures increase with increasing carbon equivalent. Hence, there might be the maximum temperature attained when changing the carbon equivalent of the samples.

In order to investigate the effect of morphology on the microwave heating of the MgO–C system, samples were pressed at 800 MPa and pelletized into a disk (12 mm diameter). The raw pelletized samples were not heated above 973 K, but the crushed samples (<150 μm) were heated probably due to the larger surface area under microwave exposure in the case of crushed samples.

Heating behavior of pressed samples of various carbon equivalent were shown in Fig. 2(b). The samples of \(C_{eq}\) less than 2 were not heated above 973 K in 10 minutes of exposure. Both the heating rate and the maximum temperature were higher than unpressed samples in Fig. 2(a). To understand the difference in the heating properties, graphite particle size of both samples were considered. Distribution of the graphite particle size in the unpressed samples, which is the same as that of the reagent graphite powder, is as follows; ~38 μm: 8.70%, 75–150 μm: 40.8%, 75–150 μm: 25.9%, 150 μm+: 24.6%. The size in the pressed samples was investigated with electron probe microanalyzer (EPMA). SEM image and X-ray images of carbon and magnesium were shown in Fig. 3. Mapping of carbon (Fig. 3(b)) shows that the size of graphite particles was smaller (<15 μm) than that of the unpressed samples. As graphite particle size was decreased and total surface area of graphite was increased by powder pressing, improvement of Joule heating of graphite might be expected. In Fig. 2(b), after increasing rapidly, the temperature increased slowly. The value of the maximum temperature was the highest in the sample of \(C_{eq}\) 3, and the heating rate was the largest in the sample of \(C_{eq}\) 4. The heating behavior in the early stage was different from that of unpressed samples, namely, heating rate didn’t increase simply with increasing carbon fraction. In the samples of...
larger carbon fraction, contact of graphite particles was increased by powder pressing, resulting the area under microwave exposure of graphite particles might decrease.

### 3.1.2 Reduction behavior

The progress of carbothermic reduction of MgO was investigated in the experimental arrangement shown in Fig. 1(b). After microwave irradiation, white powder was observed to pile up on the upper crucible and was indicated as reoxidized MgO by the detection of Mg with ICP emission spectrometry.

The unpressed and pressed samples of $C_{eq}$ 3 were treated by microwave irradiation for various processing times. The fractional reduction of MgO is shown in Fig. 4, where the pressed samples showed the higher values. This may be recognized by the differences in heating behavior and contact between MgO and graphite by powder pressing.

### 3.2 Effect of carbon equivalent

Effect of carbon equivalent in the pressed samples on their fractional reduction was also investigated. The pressed samples of $C_{eq}$ 2–5 were treated by microwave irradiation for 10 minutes. The reduction ratio obtained is shown in Fig. 5. Reduction ratio was maximum at graphite content of $C_{eq}$ 3–4. This behavior may be interpreted with the maximum temperature attained for each sample in Fig. 1(b).

### 3.3 Effect of atmosphere

The pressed samples of $C_{eq}$ 3 were treated by microwave irradiation within 10 minutes in the 300 Nml/min argon flowing system. The fractional reduction of MgO is shown in Table 1. Mg was detected in the hydrochloric acid which was set on the gas outlet side, which prored the production of Mg gas. The higher values were obtained compared with in atmospheric experiments, and this is probably because the
flowing argon gas reduced oxygen potential in the system and worked as a carrier of productive gas.

### 3.4 Treatment of MgO–C refractory brick with microwave irradiation

A MgO–C refractory brick was crushed to powder (<150μm), and subjected to the experiments. Composition of the brick is as follows; MgO 76.2 mass%, C 15.5%, Al 3.1%, Si 2.1%. Heating behavior of MgO–C brick powder is shown in Fig. 6. The sample was heated quickly and maximum temperature was higher than any other prepared samples in spite of less carbon content. The size of graphite particles in the MgO–C brick was investigated in C distribution with EPMA. SEM image and X-ray images are shown in Fig. 7. Mapping of carbon (Fig. 7(b)) shows that small graphite particles (<8μm) existed dispersively. Since the graphite particle size was observed to be smaller size than that of pressed samples, large extent of Joule heating of graphite was indicated.

The fractional reduction of the MgO–C brick samples was investigated in air atmosphere and Ar flowing system and the results are shown in Table 2. Higher fraction values were obtained compared with those for pressed samples of MgO–C mixtures, and interpreted for the heating behavior and high contactibility between MgO and graphite. The waste MgO–C refractory bricks may be promising materials as a source of Mg as long as carbon is remaining.

### Table 1 Experimental results after microwave heating of pressed samples in the argon flowing system.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fractional reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>37</td>
</tr>
<tr>
<td>A4</td>
<td>46</td>
</tr>
<tr>
<td>A6</td>
<td>40</td>
</tr>
</tbody>
</table>

### Table 2 Experimental results after microwave heating of samples of MgO–C brick.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time (minute)</th>
<th>Atmosphere</th>
<th>Fractional reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>10</td>
<td>In air</td>
<td>25</td>
</tr>
<tr>
<td>M2</td>
<td>8</td>
<td>Ar flowing</td>
<td>36</td>
</tr>
<tr>
<td>M3</td>
<td>10</td>
<td>Ar flowing</td>
<td>58</td>
</tr>
</tbody>
</table>

### 4. Summary

The MgO–C mixtures were heated with microwave irradiation of 2.45 GHz and 1600 W. The influence of factors such as powder pressing and carbon amount in the samples on the heating behavior and the reduction ratio of MgO was investigated. The results obtained are summarized as follows.

![Fig. 6](image-url)  
Time-temperature curve of the MgO–C brick mixture.

![Fig. 7](image-url)  
EPMA results for powder of MgO–C brick. (a) SEM micrograph, (b) Mg-distribution, (c) C-distribution.
(1) Initial graphite particle sizes were of great importance in the heating behavior of MgO–C system with microwave irradiation. To decrease the graphite particle sizes, powder pressing was effective.

(2) Carbothermic reduction of MgO was attained with microwave irradiation. Influence of carbon equivalent ($C_{eq}$) on the fractional reduction was investigated and maximum value was obtained in the samples of $C_{eq}$ 3–4.

(3) A significant increase in reduction rate is obtained with argon flowing in the system.

(4) Carbothermic reduction of MgO–C brick was observed, which exhibited the possibilities of practical uses of waste MgO–C refractory.

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REFERENCES