Melting Property of MgO Containing Sinter*

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Synopsis

The solution property of MgO containing materials into the CaO-Fe₂O₃ system and the melting property of MgO containing sinter during reduction were investigated. The results obtained are summarized as follows:

1. The formation of high viscosity silicate and magnetite prevents the homogenization of slag and therefore, Cr slag and Ni slag remain unslagged. The formation of dicalcium ferrite prevents the dissolution of periclase into the CaO-Fe₂O₃ system.

2. During reduction unslagged MgO makes the shell of MgO-FeO solid solution with FeO in glassy silicate and its solution is negligibly low.

3. For both normal sinter and pellet, all silicate minerals dissolve above about 1240°C.

4. MgO addition in sinter is effective to decrease the slag quantity during reduction but the melting property of sinter is not so improved as that of pellet. The proper basicity for sinter and pellet is about 1.4.

I. Introduction

Sinters with a high MgO concentration have been made recently by adding materials such as dolomite and serpentine. This purpose is mainly to prevent the decrease in fluidity of blast furnace slag, which is caused by charge of high Al₂O₃ ores. Many studies on MgO containing sinters so far reported were therefore restricted to the sintering behaviors of MgO containing materials and the effect of MgO on the low temperature characteristics of sinters such as reducibility and disintegration.

On the other hand, MgO containing pellets have been developed and it becomes clear that MgO is effective not only to decrease disintegration but to raise the softening-melting temperatures during reduction.5,7 And good operation results of blast furnaces have been obtained by use of them.6-9

The present report describes the effect of MgO with change of basicity on the softening and melting property of sinters in comparison with that of pellets.

II. Samples

Dolomite sinters and pellets prepared by industrial apparatuses and sinters by a testing pot were used as the samples. Those chemical compositions are shown in Table 1. Chemical reagents of MgO, Al₂O₃, SiO₂, CaO, Fe₂O₃, and electrolytic iron were used for the quenching experiments to study generating quantity of liquid slag and liquidus temperatures of unslagd cores of sinter and pellet.

III. Melting Behavior of Unreduced Core

1. Experimental Procedure

1. Melting Experiments of Slag Minerals

Pellets and sinters were crushed and then reduced by pure CO at 400°C for 20 min. By this treatment, hematite was reduced to magnetite, while the other minerals unchanged. The powders thus obtained were separated by using a magnet in methanol. The residual substances, exclusive of hematite and magnetite, were reduced to wustite by CO-CO₂ gaseous mixture (CO: 60%, CO₂: 40%) at 900°C. Each 0.5 g of the obtained powders enveloped in platinum foil were heated so as to reach the fixed temperature by 1 min, held them at that temperature for 10 min and then quenched in ice water. The resulting powders were identified by X-ray diffraction.

2. Melting Experiment of Unreduced Core

Sinters and pellets were reduced to wustite by CO-CO₂ gaseous mixture (CO: 60%, CO₂: 40%) at 900°C. After crushing by a disk mill, they were pressed to columnar briquets of 10 mm x 9 mm under a pressure of 650 kg/cm². They were heated with the rate of 5°C/min in N₂ using a horizontal electric furnace and the melting behaviors of the samples were photographed.

3. Quenching Experiments of the Five Components

Chemical reagents of hematite and electrolytic


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Table 1. Chemical composition of the sample sinters and pellet.

<table>
<thead>
<tr>
<th>Kinds</th>
<th>Sample*</th>
<th>Chemical component (%)</th>
<th>MgO containing material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T. Fe</td>
<td>FeO</td>
</tr>
<tr>
<td>Sinter</td>
<td>A</td>
<td>54.30</td>
<td>8.12</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>57.47</td>
<td>11.23</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>55.59</td>
<td>15.93</td>
</tr>
<tr>
<td>Pellet</td>
<td>D</td>
<td>60.61</td>
<td>&lt;0.10</td>
</tr>
</tbody>
</table>

* Sample sinter A and pellet D were made with industrial apparatus. Others were made with a testing pot.
iron were mixed to give the stoichiometrical composition of wustite. The mixture was melted and crushed, and iron existing in the sample was removed by a magnet. The obtained wustite and chemical reagents of CaO, SiO₂, Al₂O₃ and MgO were mixed to fixed ratios. Each 0.5 g of the resulting powders packed in iron envelopes were heated at 1470°C for 20 min in N₂. The sample was cooled to a fixed temperature with the rate of 15°C/min, held at that temperature for 60 min and then quenched in ice water. Minerals were identified by the use of an optical microscope, an EPMA and an X-ray diffractometer to determine the ratio of wustite and liquidus temperature.

2. Experimental Results
1. Melting Behavior of Unreduced Core

Previously we measured the permeability resistance of the packed bed of pre-reduced sinters and pellets at high temperature simulating the softening-melting zone of blast furnace, which led to the finding that it depends on the melting property of unreduced cores. Since the reduction of porous ores to wustite finishes in the early stage, the unreduced core is composed of wustite, slag minerals and silicate glass. The melting property of cores is dependent on the mineral ratios, their melting points and their dissolving behaviors into the molten slag. This induces us to study the melting property of core exactly in order to improve the high temperature property of ores.

First of all, the melting behaviors of slag minerals of cores were studied. Here, sample A of high basicity and sample B of low basicity were studied, since slag minerals differ by the basicity. When the untreated samples are reduced to wustite, the ratio of wustite is so large that it is difficult to identify the other minerals by X-ray diffractometry. This required the concentration of slag by magnetic separation. The resulting samples were quenched from the fixed temperature and the minerals were identified by X-ray diffractometry. The results obtained are shown in Figs. 1 and 2. The slag minerals of sample A are β-dicalcium silicate (shortened as C₆S) and melilite. The diffraction intensities of these slag minerals at 1200°C are still strong, but at 1220°C, most of melilite dissolves and C₆S diminishes in quantity. Dissolution of C₆S finished at 1240°C and it is composed of molten slag and a part of wustite reduced from calcium ferrite.

On the other hand, the slag minerals of sample B are low basicity are mellilite and kirschsteinite (CaFe₂SiO₅). The silicate glass melts at 1150°C which is lower than that of the sample A. Dissolution of kirschsteinite finished at 1160°C and that of mellilite at 1170°C.

The slag minerals of pellet D are mellilite and calcium magnesium silicate (Ca₇Mg(SiO₄)₄) which is dissolved as well at about 1220°C.

Next, the melting properties of the samples A, C and D were studied by heating those briquets to examine the effect of MgO on the melting property and to compare the property of pellets with that of sinters. The results are shown in Photo. 1. In the case of sample C of no MgO addition, the lower angles became smooth at 1270°C and the molten slag increased in quantity at 1280°C. On the contrary in the case of dolomite sinter A, the lower angles began to become smooth at 1300°C and the increase in the quantity of molten slag caused deformation at 1320°C, which is about 40°C higher than that of sample C. Besides the same state is reached at higher temperature for pellet D, namely the change hardly occurred till 1320°C and it began to deform a little at 1330°C.

2. Liquidus Temperatures and Ratios of Wustite of the Five Components System

As described above the permeability resistance of

![Fig. 1. X-ray diffraction figures with Cu Kα radiation of sinter A reduced to wustite after magnetic separation.](image1)

![Fig. 2. X-ray diffraction figures with Cu Kα radiation of sinter B reduced to wustite after magnetic separation.](image2)
the softening and melting zone of blast furnace depends on the melting property of unreduced cores of ores. And slag minerals dissolve in the molten slag at this temperature, which led to the fact that the change of unreduced cores is attributed to the melting property of the five components system of FeO, CaO, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and MgO.

Thereupon liquidus temperatures and quantities of molten slag were studied from the change in quantity of wustite by basicity corresponding to those of pellets and sinters under constant quantity of Al\textsubscript{2}O\textsubscript{3} and MgO. For instance, weight percent of wustite becomes 75.0 for sinter A reduced to wustite under the assumption that the composition of FeO is constant. In the same way it becomes 85.4\% for pellet D. Experiments were made for two levels. One corresponds to the sinter level where weight percent of FeO was 75.0, that of Al\textsubscript{2}O\textsubscript{3} 3.0, that of MgO 3.0, and that of the sum of CaO and SiO\textsubscript{2} 19.0, while the basicity was changed from 0.43 to 2.33. The other is based on the pellet level where weight percent of FeO was 85.0, that of Al\textsubscript{2}O\textsubscript{3} 1.8, that of MgO 1.8, and that of the sum of CaO and SiO\textsubscript{2} 11.4, while the basicity was changed from 0.5 to 2.0. In these experiments all primary crystals were wustite. In addition X-ray diffractometry was not applied to determine liquidus temperatures since dendritic wustite precipitated from molten slag.

The resulting liquidus temperatures for the two levels are shown in Figs. 3 and 4. Figure 3 reveals that the liquidus temperature shows the minimum value of 1362°C at the basicity of 0.43 and increases with increasing basicity till the basicity of 1.5. It becomes the nearly constant value of 1430°C in the basicity range of 1.5 to 1.9 but it decreases when the basicity increases more than 1.9. Figure 4 shows the same trend, namely, liquidus temperature increases with increasing basicity in the range of 0.5 to 1.4 but above this range it decreases with increasing basicity.

Next the ratio of molten slag was examined. In these experiments all primary crystals were wustite and only wustite and silicate glass existed above 1300°C. In this experiment the ratio was evaluated by the following method\textsuperscript{14}\textsuperscript{15}, since minerals were homogeneous and their compositions were nearly equal to those of equilibrium state although a chemical analytical method\textsuperscript{14} can be applied as well. Minerals were evaluated by the point analysis using EPMA and their ratios were calculated from Eq. (1) by taking the materials balance obtained by the least squares method.

\[
C_i = \sum_j \alpha_{ij} \cdot x_j \quad \text{..................}(1)
\]

$C_i$: a weight ratio of chemical composition
Fig. 5 gives the ratios between wustite and silicate glass at 1300°C for the sinter level. The maximum ratio of wustite is about 55% at the basicity of 1.0, while there is a little difference between them in the basicity range of 0.66 to 1.9. Except this range, the ratio of wustite decreases, particularly, at low basicity.

Figure 6 shows the mineral ratio at 1300°C for the pellet level. This indicates that the ratio of wustite has a nearly constant value of 65% in the basicity range of 0.7 to 2.0.

3. Discussion

When pellets and sinteres are charged into a blast furnace, they are reduced from the outside of particles. And the outer shell of the particle is composed of metallic iron, wustite and slag minerals, while the inner core is composed of wustite and slag minerals. When it is heated at high temperatures, metallic iron becomes to form large continuous crystals by sintering, which leads to prevent the diffusion of reducing gas into inner cores and to retard reduction. At the softening and melting zone, the molten slag generates in the unreduced cores of ores and the load on ores causes the exudation of slag containing wustite to its surface.

Vacant spaces between ores are filled with this molten slag at the softening and melting zone. This causes the decrease of fractional void volume to produce a high pressure drop.

On the contrary, it is said enough to consider hematite, magnetite, hemicalcium ferrite, C2S, melilite, iron gehlenite and silicate glass as the principal minerals of fluxed sinters. Sasaki et al. revealed that hemicalcium ferrite of commercial sinters is reduced to a fine mixture of magnetite and slag minerals, and is further changed to a mixture of wustite and slag minerals.

Consequently unreduced cores of sinters are composed of slag minerals, silicate glass and wustite reduced from hematite, magnetite and hemicalcium ferrite at the shaft of blast furnace. Molten slag begins to be generated in the cores of sinters with descending through the shaft and increasing temperature. And minerals dissolves in this slag to increase the quantity.

Figure 1 indicates that silicate glass melts first between 1200°C and 1220°C, then, parts of melilite, C2S and wustite dissolve at 1220°C. And at 1240°C the increase of solubility allows to dissolve all C2S. This generating path of molten slag should be considered on the basis of the phase diagram as follows:

Fig. 5. Change of mineral ratio of five components system at 1 300°C.

Fig. 6. Change of mineral ratio of five components system at 1 300°C.
the point analysis of many wustites by EPMA shows an almost uniform composition. Chemical compositions of hematite, magnetite and hemicalcium ferrite differ from one another and they vary even in the same minerals, which are kept to wustite. However, the melt formation makes wustites composition uniform. We should consider the similar eutectic melt formation process for B and D. For this reason in the case of discussion of melting behavior above about 1240°C of the softening and melting zone of blast furnace where no slag minerals of sinters and pellets exist, it is sufficient only to consider that chemical compositions of cores independent of the kind and quantity of minerals.

The curve of liquidus temperature in Fig. 3 differs from that of the ratio of wustite in Fig. 5. For instance the value of the ratio of wustite reaches a maximum at the basicity of 1.0, while that of liquidus temperature at the basicity of 1.5. Consequently molten slag increases more rapidly above 1300°C at the basicity of 1.0 than at that of 1.5. It is proper basicity where ores have high values of both the ratio of wustite during increasing temperature and liquidus temperature. In this sense industrial sinters and pellets are found to be produced at almost optimum basicity.

Value of the ratio of wustite at 1300°C for a sample of FeO 75.0, Al2O3 3.0, CaO 13.2, and SiO2 8.8wt% was about 19%, which led to the finding that MgO decreased the solubility of FeO in the melt.

For the above reasons the result of Photo. 1 will be considered as follows:

The melting property of sinters is improved greatly but the effect of MgO becomes smaller on sinters than on pellets since larger amount of FeO dissolves in slag because of greater quantity of gangue, and minerals containing MgO remains unslagged, which will be discussed in the next.

IV. Behavior of MgO during Sintering and Reduction

1. Experimental Procedure

1. Solution Experiments of MgO Containing Materials

It has been examined the solution property of MgO containing materials in the CaO–Fe2O3 system which should exist to a great extent in sinters. First of all, chemical reagents of Fe2O3 and CaO were mixed to be fused in a ratio of 85wt% to 15wt%. The slag obtained was crushed and packed around MgO containing materials in Pt envelopes. They were heated at 1350°C for 10 min with an electric furnace in air and were quenched in ice water.

2. Behavior of Unslagged MgO during Reduction

Effect of unslagged MgO on the melting behavior of a core was studied. First wustite sinter A was heated at 1220°C and then quenched. Its silicate glass was analyzed by EPMA. To obtain slag of the same chemical compositions, wustite was mixed with chemical reagents in the ratio of FeO 40wt%, CaO 30wt%, SiO2 23wt%, and Al2O3 7wt% and heated it at 1470°C in N2. This was crushed and packed around reagent grade MgO which was pressed to a mass under a hydrostatic pressure of 3000 kg/cm². They were wrapped in an iron envelope and heated at 1220°C for 20 min in N2 with an electric furnace, then, quenched in ice water.

2. Results and Discussion

1. Solution Property of MgO Containing Materials

It is well known that the sintering process depends on both the generating order and property of melt. And two paths have been considered for the melt.
formation, namely, the one is Olivine while the other calcium ferrite.\textsuperscript{16} Besides, the experiment of simplified composition system has revealed that the reaction between Fe\textsubscript{2}O\textsubscript{3} and CaO is the most liable to occur and gangue minerals dissolve in it.\textsuperscript{17} On the other hand, MgO containing materials are difficult to react and apt to remain as intermediate products.\textsuperscript{4} In the present paper the solution property of MgO containing materials such as Ni slag, Cr slag and dolomite into the CaO–Fe\textsubscript{2}O\textsubscript{3} system was studied.

Photograph 3(1) shows X-ray images of the representative boundary texture of Cr slag in the slag obtained by EPMA. Cr slag is composed of forsterite (2MgO·SiO\textsubscript{2}) and spinel (MgO·Al\textsubscript{2}O\textsubscript{3}) which remain unslagged as large crystals as shown by No. 1 and No. 3 in Table 2. Besides, a heavy element is considered to be present at the black periphery of spinel, which would be made by the exchange of Al\textsuperscript{3+} ions of spinel with Fe\textsuperscript{3+} ions of the slag as indicated by the analytical value of No. 2. For this reason the solution property of spinel is bad and forsterite dissolves mainly as is indicated by the analytical value of No. 4. And magnetite, concentrating MgO and Al\textsubscript{2}O\textsubscript{3}, precipitates from the CaO–Fe\textsubscript{2}O\textsubscript{3} slag.

Ni slag also remains unslagged. It is composed of forsterite and enstatite (MgO·SiO\textsubscript{2}) and enstatite (MgSiO\textsubscript{3}).

![Photograph 3(1) shows X-ray images of the representative boundary texture of Cr slag in the slag obtained by EPMA.](image)

**Table 2.** Analytical results of the quenched mixture of MgO-containing material and calcium ferrite by X-ray microanalyzer.

<table>
<thead>
<tr>
<th>Photo. No.</th>
<th>No.</th>
<th>Analyzed phase</th>
<th>As oxide (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MgO</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>Spinel (center)</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Spinel (periphery)</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Forsterite</td>
<td>56.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Silicate glass</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Magnetite</td>
<td>19.1</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Forsterite</td>
<td>56.6</td>
</tr>
<tr>
<td></td>
<td>7</td>
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<td>8</td>
<td>Magnetite</td>
<td>14.7</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>Dicalcium ferrite</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Ferrite glass</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* as Fe\textsubscript{3}O\textsubscript{4}
dissolves selectively at the interface and so only forsterite remains. In this case also magnetite, highly concentrating MgO, precipitates from the melt. When Cr and Ni slag dissolve in the CaO-Fe₂O₃ system, the formation of high viscosity slag containing much SiO₂ and precipitated magnetite prevent the homogenization in this manner. Hence, the solubility of slag reaches saturation for forsterite and it would be left unslagged.

In the case of dolomite sinter it is known that MgO remain unslagged as periclase.⁴¹ On the other hand, it is known that CaO dissolved at 1320°C in the CaO-Fe₂O₃ slag composed in the ratio of 20 to 80 wt%, while MgO hardly does so since it reacts with Fe₂O₃ in the slag to make the shell of MgO·Fe₂O₃ around itself.¹⁸ The scanning image of Photo. 3(3) shows that two other phases are present except the white spherical periclase. The analytical value of No. 9 indicates light gray phases as dicalcium ferrite (2(Ca, Mg, Fe)O·Fe₂O₃), while that of No. 10 denotes dark gray phases as calcium ferrite melt. At first dolomite was heated to decompose into MgO and CaO. CaO dissolves selectively in the slag, while MgO did not so. CaO dissolved decreased the activity of Fe₂O₃ in the CaO-Fe₂O₃ melt to prevent the formation of MgO·Fe₂O₃, and MgO began to dissolve. MgO and CaO continued dissolving to make dicalcium ferrite precipitate, then, the solution of MgO would scarcely occur. As mentioned above MgO containing materials remain unslagged since the generating melt is difficult to become homogene-ous during the solution process. This requires that the grain sizes of MgO containing materials should be as small as possible and they should be mixed uniformly.

2. Behavior of Unslagged MgO during Reduction

As mentioned above parts of MgO containing materials are inclined to remain unslagged. The resulting periclase in the matrix is said to decrease the low temperature strength.⁴ The present report describes the effect of unslagged MgO on the softening and melting property of ores during reduction.

Photograph 4 shows the images by the current and characteristic X-rays of EPMA of the quenched samples. Table 3 shows the results by point analysis of the present phases. The solid solution of MgO-FeO varying continuously in composition are formed around the MgO grain as shown by the images of the characteristic X-ray of Fe and Mg of Photo. 4. And at the outside of this phase a solidified slag layer containing CaO and SiO₂ for 11% shown by No. 2 is present. Besides they are surrounded by a layer of C₃S among which little gehlenite (2CaO·Al₂O₃·SiO₂) of the composition of No. 4 was located. Wustite dissolving MgO for 3% precipitates from the original slag in which MgO scarcely dissolves as shown by the value of No. 6.

Consequently at first MgO makes MgO-FeO solid solution of high melting point at the slag/MgO interface through which MgO diffuses to dissolve in the slag. CaO, SiO₂ and Al₂O₃ move to the slag bulk due to the combination of MgO and FeO after MgO
dissolving in the slag. The rest of melts is, then, considered to solidify after the precipitation of C2S and gehlenite. For this reason MgO scarcely dissolves.

Like this MgO containing materials are inclined to remain unslagged in sinters which scarcely dissolve at high temperatures in a blast furnace which results in little effect to increase the softening and melting temperature for the amount of MgO.

V. Conclusion

The solution property of MgO containing materials into the CaO–Fe2O3 system and the effect of unslagged MgO at the high temperature zone of a blast furnace were studied. And this report describes the effect of basicity on liquidus temperatures and the ratio of melt at 1 300°C for the two levels of FeO of FeO–CaO–SiO2 A12O3MgO system.

1) Spinel of Cr slag does not proceed to dissolve since it reacts with Fe3+ ion in the slag to form the shell of MgO•(Al, Fe)2O4. When Cr and Ni slag dissolve in the CaO–Fe2O3 system, the formation of high viscosity slag and precipitated magnetite prevent the homogenization. Periclase remain in the slag due to the formation of dicalcium ferrite after decomposition of dolomite. For this reason low temperature strength of sinters decreases with MgO addition.

2) Unslagged MgO does not improve the high temperature property of ores since it makes the shell of solid solution of MgO–FeO at the boundary with slag and scarcely dissolves.

3) MgO addition is less effective for sinters than for pellets while it is valid to decrease the quantity of generating melt. And low temperature disintegration is improved since MgO promotes the dissociation of hematite to magnetite. For these reasons MgO addition is effective to improve the quality of sinters.

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17) F. Matsumo: Tetsu-to-Hagane, 64 (1978), 1499.