Changes of Mineral Phases during the Sintering of Iron Ore–Lime Stone Systems*

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Synopsis
In order to elucidate the fundamental aspects of the sintering processes of self-fluxing sinters, the mineral formation processes of mixtures of iron ore and lime stone with or without coke were studied. After heating between 1200° and 1350°C the sinters were examined by microscopy, X-ray diffraction and EPMA.

The results indicated that the mineral formation processes of the systems were fundamentally the same as those of 80%Fe₂O₃-CaO-SiO₂ system reported earlier. They were as follows:
1. Molten calcium ferrite was formed at the beginning.
2. Gangue minerals dissolved into the melt.
3. Iron oxides were precipitated. They were either or both of hematite and magnetite, depending on the oxygen potential or the SiO₂ content of the melt.
4. At higher temperatures, solid iron oxides and a melt coexisted, and characteristic microstructure was formed during solidification depending on the basicity.

On the basis of the above results, the microstructures and the formation processes of self-fluxing sinters with various basicities were discussed.

I. Introduction
It has been reported that the metallurgical properties of self-fluxing sinters, such as the mechanical strength, the degradability, the reducibility at around 550°C, and the reducibility at high temperatures, are greatly dependent on minerals consisting of them. Accordingly, an elucidation of the fundamental aspects of the physical and chemical nature of the sintering processes, especially the mineral formation processes, is required in order to control the qualities of self-fluxing sinters.

Although comprehensive works have been done on this problem, many phenomena in the mineral formation processes have been left unsolved. One of the authors studied this problem basically through the sintering of very simple mixtures consisting of reagents, and several bits of interesting information have been obtained especially on the formation processes of the secondary or granular hematite, a product detrimental to the degradability. However, many complications can be expected on the mineral formation processes in iron ore–lime stone systems, because their chemical compositions and mineral constituents are very complex. Therefore, several iron ore–lime stone systems are examined in this study.

II. Experimental Methods

1. Raw Materials
Lime stone, coke and seven kinds of iron ore were used. Each of them was crushed into powder, whose particle size was less than 0.125 mm in diameter. Chemical compositions, main phases of iron oxides, and gangue minerals consisting of each kind of iron ores used were tabulated in Table 1.

2. Methods of Sintering and Examination
Mixtures of iron ore and lime stone were prepared. The contents of lime stone in the mixtures were 5.0, 8.5, 12.0 and 18.0 wt% as CaO constituent. Coke powder was added to some of the mixtures in order to examine the influence of the oxygen potential on the mineral formation processes. The coke content was 0.5 wt%, which was determined in a preliminary experiment.

About 15 g of a mixture was pressed by means of a steel piston in a steel cylinder of 15 mm inside diameter to a tablet of 15 mm dia. and 10 mm thick.

Table 1. Chemical compositions and main minerals of iron ores examined.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical compositions (wt%)</th>
<th>Mineral compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T. Fe</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Rio Doce</td>
<td>65.0</td>
<td>5.6</td>
</tr>
<tr>
<td>Algarrobo</td>
<td>58.5</td>
<td>8.9</td>
</tr>
<tr>
<td>MBR</td>
<td>68.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Mt. Newman</td>
<td>63.0</td>
<td>6.4</td>
</tr>
<tr>
<td>Hamersley</td>
<td>62.2</td>
<td>5.6</td>
</tr>
<tr>
<td>MIFERMA</td>
<td>60.9</td>
<td>10.7</td>
</tr>
<tr>
<td>Goa</td>
<td>59.3</td>
<td>3.9</td>
</tr>
</tbody>
</table>

** Qu: Quartz, Kao: Kaolinite, Feld: Feldspar, Gib: Gibbsite.

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These tablets were inserted into an electric furnace and heated up to 1200°, 1250°, 1300° and 1350°C in air. After holding at each temperature for about 10 min, they were taken out from the furnace and cooled.

Temperature measurements during the heating were carried out by a Pt-Pt 13%Rh thermocouple of 0.2 mm diameter inserted near the tablets.

Each of the sintered tablets was examined by microscopic observation and some of them by X-ray diffraction and EPMA.

**III. Experiments and Results**


The microstructures of sintered samples were classified into four different types. The first one (type-I) consists of calcium ferrite, unmelted iron oxides, and gangue minerals. The second one (type-II) consists of calcium ferrite, secondary or granular hematite, and dicalcium silicate. The third one (type-III) consists of calcium ferrite and dicalcium silicate. The last one (type-IV) consists of glassy slag and secondary or granular hematite. The microstructures of iron ore–lime stone systems examined are summarized in Fig. 1. It shows that almost all the microstructures of various mixtures belonged to type-I at the beginning of heating and that they changed from type-I to another type with increase in temperature. Most of the microstructures of mixtures with high basicities (the ratio of %CaO to SiO₂) changed from type-I to either type-II or type-III. In some mixtures, the microstructure of type-III was formed from type-I by way of type-II. In case of mixtures with low basicities, the microstructures changed from type-I to type-IV with increase in temperature.

As a typical example of mixtures with high basicities, microstructures of a mixture of iron ore (Mt. Newman) and 12%CaO are shown in Photo. 1. The photograph shows the structure changes in the following way with increase in temperature.

1. Specimen heated up to 1200°C: The microstructure belongs to type-I. Caustic lime (CaO) originated from lime stone is no longer observed and all of the CaO constituent exist as calcium ferrite which surrounds the unmelted iron ore particles. Most of the gangue minerals still remain.

2. Specimen heated up to 1250°C: The microstructure belongs still to type-I. However, more calcium ferrite has been formed and a small quantity of dicalcium silicate (2CaO·SiO₂) is observed in the calcium ferrite. On the contrary, particles of unmelted iron ore and gangue minerals has decreased in number and size.

3. Specimen heated up to 1300°C: The microstructure belongs to type-II. A very small quantity of gangue minerals still remains. Few unmelted particles of iron oxide (hematite) remain, whereas the formation of granular hematite particles has occurred. Calcium ferrite and dicalcium silicate has increased furthermore in quantity. The latter phase is observed distinctly within the former phase as needle-like minerals with dark gray color.

4. Specimen heated up to 1350°C: The microstructure belongs to type-II. Typical granular particles of hematite has increased in number and size. The eutectic structure consisting of calcium ferrite and dicalcium silicate is observed among the granular hematite particles. Particles of raw materials such as iron oxides and gangue minerals are no longer observed.

As a typical example of mixtures with low basicities, the microstructures of the iron ore (MIFERMA)–12%CaO mixture are shown in Photo. 2. The photograph shows the microstructure changes of minerals with increase in temperature in the following way.

1. Specimens heated up to 1200° and 1250°C: The microstructures of both specimens belong to type-I. A small quantity of glassy slag is formed locally in the specimen heated up to 1250°C.

2. Specimens heated up to 1300°C and above: The microstructures belong to type-IV. At temperatures higher than 1300°C, gangue minerals and calcium ferrite are no longer observed. A small quantity of dicalcium silicate is observed in the specimen heated up to 1300°C. However, in the specimen heated up to 1350°C, its quantity decreases further.
thermore, and the microstructure becomes typical of type-IV, hematite granules being dispersed in the glassy silicate slag.

The other systems showed similar formation processes of minerals as those shown in either Photo. 1 or Photo. 2 depending on the basicity, although the transformation temperature from type-I to another was different to some extent from one mixture to another.


1. Preliminary Study

The quantity of coke, which was intended to be added in the iron ore–lime stone systems, was determined by the following preliminary study. A mixture of iron ore (Mt. Newman) and 12\%CaO was prepared and divided equally into three. Adequate amounts of coke powder were mixed into each of them.

Photo 1.
Microstructure changes of iron ore (Mt. Newman)–lime stone (12\%CaO) system.

Photo 2.
Microstructure changes of iron ore (Mt. Newman)–lime stone (12\%CaO) systems.
so that their coke contents were 0.5, 1.0, and 3.0%, respectively. Tablets made from them were heated up to 1300°C in air and the phases of iron oxide were mainly studied.

In the specimen with 3% coke, metallic iron and wustit (FeO) were formed by reduction during heating. In the specimen with 1% coke, the iron oxide phase was magnetite. In the specimen with 0.5% coke, both hematite and magnetite were formed. In case of the usual sinters, both magnetite and hematite are formed. Accordingly, the coke content to be added was determined as 0.5wt% in this study.

2. Changes of Microstructures of Iron Ore–Lime Stone–0.5% Coke Systems

Iron ores used were Mt. Newman, Hamersley and MIFERMA. Mixtures of iron ore–8.5%CaO–0.5% coke and iron ore–12%CaO–0.5% coke were prepared. They were pressed into tablets and heated up to 1200°C, 1250°C, 1300°C and 1350°C in air. After cooling, the microstructures were examined.

The microstructures of these systems were observed to change with temperature approximately in the same way as the systems without coke. Typical examples of the microstructure change were shown in the following.

The iron ore (Mt. Newman)–12%CaO–0.5% coke system showed a microstructure change typical for mixtures with high basicity as shown in Photo. 3. Photographs 3(A) and (B) show that the microstructures of the specimens heated up to 1250°C belong to type-I. In the specimen heated up to 1300°C and above, microstructures consist of calcium ferrite, dicalcium silicate, hematite, and magnetite as shown in Photos. 3(C) and (D).

The microstructures of the iron ore (MIFERMA)–12%CaO–0.5% coke system are shown in Photo. 4, as an example of the typical microstructure change of systems with low basicity. The microstructure of a specimen heated up to 1200°C belongs to type-I, although the formation quantity of calcium ferrite is small. In specimens heated up to 1250°C and above, the microstructures consist of hematite, magnetite, and glassy silicate slag. At 1250°C, the quantity of hematite is small and it increases with increase in temperature. The size of particles of hematite and magnetite also increases with increase in temperature.

The other systems showed a process similar to those without coke, with an exception that magnetite was formed together with hematite.

3. Chemical Compositions of Minerals

Specimens heated up to 1250°C and 1350°C in air were examined by EPMA. A line analysis was carried out on them and the average chemical composition of each mineral was determined quantitatively by averaging the observed X-ray intensities of several grains of the same mineral.

Several examples of the average chemical composition determined are shown in Table 2. In granular hematite, small quantities (less than 1%) of SiO₂, CaO and Al₂O₃ were detected. The calcium ferrites contained a few percent of SiO₂ and Al₂O₃. The main constituents of the glassy slag were Fe₂O₃ (about 20%), CaO and SiO₂. The ratios of CaO to SiO₂ of glassy slag were similar to those of the mixtures. A few percent of Al₂O₃ was also detected in glassy slags. In the eutectic mixtures consisting of fine crystals of calcium ferrites and dicalcium silicate, the average compositions of Fe₂O₃, CaO, and SiO₂ were similar to those at the ternary eutectic point in the Fe₂O₃–CaO–SiO₂ system.³³)

The Al₂O₃ constituent in granular hematite has
been reported to have detrimental effects on the degradability.20 Therefore, they were examined in relation to those of minerals surrounding the granular hematites. The results are summarized in Fig. 2. As was expected, the Al₂O₃ contents in the granular hematites increased with increasing of those in minerals surrounding the granular hematites. The Al₂O₃ contents in the hematites surrounded by calcium ferrites and dicalcium silicate were greater than those surrounded by glassy silicate.

**IV. Discussion**

As reported earlier, the mineralogical changes of the 80%Fe₂O₃-CaO-SiO₂ ternary system during heating proceeded in the following three fundamental stages.

1. Calcium ferrite was formed by reaction between hematite and caustic lime.
2. As a melt of calcium ferrite was formed, quartz dissolved into it.
3. After the assimilation of quartz into the melt, the microstructure of solidified melt depended on its basicity.

In comparison with the above process, let us con-
sider the mineralogical changes of the iron ore–lime stone systems. It is certain that the first stage and the second stage took place in all the iron ore–lime stone systems examined, because most of the microstructures of specimens heated up to 1 200°C belonged to type-I, showing the state in progress of assimilation between the melt of calcium ferrite and the gangue minerals. The third stage observed in a ternary system is considered to correspond to the transformation from type-I to another type. Namely, in case of systems with low SiO$_2$ contents, the microstructures transformed from type-I to either type-II or type-III. In case of systems with high SiO$_2$ contents, the transformation from type-I to type-IV took place with increase in temperature. Therefore, it is reasonable to consider that the mineralogical changes in the iron ore–lime stone system during heating progressed in nearly the same course as the ternary system, although there were some differences between the two systems.

During the firing of sinters and pellets, it has been reported that a reaction between caustic lime and SiO$_2$ takes place in the early stage. However, in the present systems examined, most of the mineralogical changes proceeded by assimilation of gangue minerals into the melt of calcium ferrite. Accordingly, it is natural to consider that the reaction between caustic lime and SiO$_2$ in the early stage of heating had an insignificant effect on the mineralogical change.

One of the differences between the iron ore–lime stone system and the ternary system reported earlier is that the temperature of the former for complete assimilation between gangue minerals and molten calcium ferrite was higher than that of the latter system, not withstanding that the former was heated or cooled more slowly than the latter. It is assumed that the difference was caused by either or both of the following reasons.

1) Gangue minerals in iron ores were different from quartz.

2) The size range of gangue mineral particles was very wide. Quartz used in the study of the ternary system was a reagent and its particle size was less than 10 μm. Since quartz was contained in most iron ores used, as shown in Table 1, it can be considered that the first reason mentioned above was of little significance. Iron ores were used after crushing into powder whose particle size was less than 125 μm in diameter. So, the size distribution of gangue minerals was also expected to be the same. Therefore, the second reason is more probable for the difference of the microstructure transition temperatures between the ternary system and the present system. This kind of difference took place, as shown in Fig. 1, among the iron ores used containing the same kind of gangue minerals. This may be caused mainly by the second reason described above.

Another difference between the ternary system and the present system is seen in the chemical composition of minerals formed. As shown in Table 2, small quantities of Al$_2$O$_3$ and SiO$_2$ were contained in hematite and calcium ferrite, which are main minerals consisting of sinters. The values obtained in this study were nearly equal to those of the minerals in sinters reported by Sasaki et al. and Nakazawa. Sasaki and Nakazawa considered the calcium ferrite containing a few percent of Al$_2$O$_3$ as hemi-calcium ferrite, different from the assumption by Bogdan and Worner that it is CaO·Al$_2$O$_3$·2Fe$_2$O$_3$. However, X-ray diffraction patterns of this kind of calcium ferrite were slightly different from those of CaO·2Fe$_2$O$_3$. So, the problem is not entirely solved.

Hematite in sinters has been said to originate in several different sources and processes. Most commonly, it has been considered that hematite is formed through crystallization directly from melt, or it is a residue from incomplete assimilation of ores. Other processes of the hematite formation have been proposed. Some of them are as follows:

i) Oxidation of magnetite suspended in the melt

ii) Oxidation of magnetite in the solid sinter

iii) Phase changes in the solid state during cooling.

The third process has been used in explanation of the formation of hematite named "skeletal rhombohedral hematite" or "multi-component hematite" which is said to cause detrimental degradation during reduction at temperatures around 550°C.

Harbord and Goldring have summarized three formation processes of iron oxides in sinter as follows:

i) Process before the onset of melt formation: solid/gas reactions

ii) Process in existence of melt: (a) solid/melt reactions; (b) crystallization from melt

iii) Post-solidification process: (a) solid/gas reactions; (b) phase changes in solid during cooling.

Among these processes, they have concluded that the solid/melt reactions are of little importance in the sinters. However, one of the authors has illustrated from the study of the calcium ferrite–quartz system that granular hematite can be formed in a solid/melt reaction, namely quartz/melt of calcium ferrite reaction. In the present iron ore–lime stone systems, the solid/melt reaction, namely the assimilation of gangue minerals into the melt of calcium ferrite, was also of importance in the mineral formation processes.

A remarkable solid/melt reaction was observed in the systems with larger SiO$_2$ contents. In this reaction calcium ferrite was formed as an intermediate product and consumed with increase in temperature, resulting in the formation of iron oxide suspended in silicate melt. This reaction also takes place in systems without quartz. This means that a condition for occurrence of the above-mentioned reaction is satisfied by gangue minerals containing SiO$_2$ such as kaolinite and feldspar.

In raw materials of the iron ore–lime stone system examined, iron oxides are much more than gangue minerals. Reactions between iron oxides and caustic lime are expected to occur easily, as reported earlier. Accordingly, the microstructure may be considered to be dependent mainly on the degree of completion of the reaction between gangue minerals and calcium ferrite melt.
A comparison between systems with coke and without coke was made and different iron oxide phases have been recognized depending on the quantity of coke added. In this study, most of coke was assumed to be consumed in reducing reaction because little air was expected to flow in and oxidize the coke. Accordingly, if the quantity of coke was enough, hematite in the systems might be reduced into wustit. This was confirmed by a preliminary study using a mixture with 3% coke, in which not only wustit but also iron was formed after heating. As wustit and magnetite, different from hematite, have a large reactivity with gangue minerals, another mechanism for the mineral formation can operate at the local points in a sinter where the omnipresence of coke occurs. However, such a mechanism operates only at local points because hematite in sinters was reported to be about 20 to 40% in weight, even though 5% coke was added.

In systems with 0.5% coke, formation of calcium ferrite took place at the beginning as shown in Photos. From microstructure observations, it is considered that the gangue mineral/calcium ferrite melt reaction produces a coexisting state of solid and liquid. In case of systems with high basicity, the solid consists of magnetite as shown in Photo. 3. In contrast to this, the solid consists of hematite and magnetite in case of systems with low basicity. From liquid systems with high basicity, calcium ferrite and dicalcium silicate are formed on solidification and glassy silicate is formed from liquid systems with low basicity. The mineralogical changes mentioned above essentially hold also in systems without coke, except for the iron oxide phases.

The above discussion leads to a conclusion of Fig. 3 for mineral formation processes of the iron ore-lime stone system. As reported earlier, the reaction rate between hematite and caustic lime becomes faster with increase in temperature. Moreover, as is evident from the chemical formula, the quantity of hemihematite formed is approximately 5.7 times as much as that of caustic lime added, if the reaction proceeds completely. These two factors indicate that the mineral formation processes in Fig. 3 are predominant in the systems examined.

The mineral formation processes shown in Fig. 3 is characterized by the reaction between calcium ferrite melt and gangue minerals containing SiO₂. On the basis of the Fe₂O₃-CaO-SiO₂ ternary phase diagram, observed mineralogical changes are discussed in the following under the assumption that any other constituents such as Al₂O₃ and MgO have no effects on the changes. This assumption is considered to be reasonable because their contents are small as shown in Table 1.

At 1400°C the mixture of 90%Fe₂O₃ and 10%CaO consists of magnetite and the melt at composition "l" in Fig. 4. In the following we consider that SiO₂ is added little by little into this system at 1400°C till the mean composition reach "N" (81%Fe₂O₃, 9%CaO, 10%SiO₂) in Fig. 4. With the dissolution of SiO₂ into the melt, the composition of the melt would change along the liquidus surface of 1400°C, or curve l-m-n in Fig. 4. At the same time, the mean composition of the system would change along the straight line L-M-N. The lever rule shows that the quantity of magnetite varies from the initial value lL/nH to the final value nN/nH. This means that magnetite increases in quantity with the dissolution of SiO₂ into the calcium ferrite melt. If the dissolution takes place...
in the hematite phase, hematite will precipitate and its quantity will increase in the same way as mentioned above. In this way the mechanism for precipitation of iron oxides by reaction between calcium ferrite melt and gangue minerals containing SiO₂ can be understood on the basis of the phase diagram. The reason why this mechanism operates during heating is, after all, attributed to the fact that the formation of calcium ferrite occurs most easily.

V. Summary

In order to elucidate the fundamental aspects of the mineral formation processes in self fluxing sinters during firing, several iron ore-lime stone systems with no coke and with 0.5% coke were studied. The results obtained are summarized as follows:

1. The mineral formation processes are essentially the same as that in 80%Fe₂O₃·CaO·SiO₂ system reported earlier.²²

2. The processes were characterized by the reaction between gangue minerals containing SiO₂ and calcium ferrite melt.

3. As the reaction proceeded, calcium ferrite was consumed and iron oxides were precipitated in the melt. The phase of iron oxide was dependent on the oxygen potential of the melt.

4. After the assimilation of gangue minerals into the melt, solidification of the melt led to the following microstructures. In case of systems with high basicity, the solid consisted of magnetite, calcium ferrite and dicalcium silicate. In case of systems with low basicity, it consisted of hematite, magnetite (in case of the systems with 0.5% coke) and glassy silicate.

5. Observed processes could be explained on the basis of the phase diagram.

6. Minor elements in the systems such as Al₂O₃ and MgO had little effects on the mineral formation process.

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