Reaction between Iron Oxide and Gangue Minerals at 1 373 K under Ar Atmosphere

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Generally, reactions and forming phases during ironmaking can be thermodynamically predicted using equilibrium phase diagram. However, at low temperature it will likely to be different from predicted phases and deviate from equilibrium. Hence, knowledge of solid state reaction at low temperature is required to control the melting behavior of slag phase in blast furnace. Reactions between iron oxide and gangue minerals in ore at 1 373 K under Ar atmosphere were investigated in present work.

KEY WORDS: reaction; phase; iron oxide; gangue; minerals.

1. Introduction

Suppression of CO₂ discharged from iron- and steel-making companies is an example of the biggest issues for the protection of global environment and sustainable growth of steelmaking industry. One of the ideas to decrease CO₂ emission and energy consumption from ironmaking process is to decrease the average process temperature during ironmaking. If it is possible to produce iron at lower temperature, reaction during the process may differ from the present process. Generally, reactions and forming phases during ironmaking can be thermodynamically predicted using equilibrium phase diagram. However, at low temperature the phases will likely to be different from predicted phase and deviate from equilibrium. Raw materials charged into blast furnace includes various minerals or crystal phases. Behavior of slag formation can’t be estimated without considering the initial form, type of crystal phase and reaction between solid minerals and solid iron oxides at low temperature. Hence, knowledge of solid state reaction at low temperature is required. Fundamental reactivity between iron oxide and gangue minerals in ore at 1 373 K under Ar atmosphere were investigated in present work.

2. Experimental

Samples were prepared by the following procedures. FeO was made by heating reagent grade Fe₂O₃ at 1 200 K for 2 hours under CO₂–50 COvol% gas. Fe₂O₃ was made by heating reagent grade Fe₂O₃ at 1 000 K for 1 hours under CO₂–20 COvol% gas. CaO was made by heating reagent grade CaCO₃ at 1 100 K for 4 hours under air. Also, reagent grade Fe₂O₃, SiO₂, Al₂O₃, MgO was used for experiments. Average particle size for FeO, Fe₂O₃, Fe₃O₄, CaO, SiO₂, Al₂O₃ and MgO was 17 µm, 17 µm, 20 µm, 15 µm, 40 µm, 45 µm and 15 µm, respectively. Oxides were mixed at same weight ratio and weighed 1 g was pressed into φ10 mm tablet shape. Oxide tablet was placed on Al₂O₃ boat and the sample was placed in a horizontal silica tube (O.D. 25 mm, I.D. 21 mm, L. 900 mm)) inside an electric resistance furnace. The sample temperature was heated at 1 373 K under Ar flow of 0.05 L/min for 60 min. The purity of Ar was 99.9999% and was dehydrated by molecular sieve during experiment. Then the sample was quenched by pulling out the horizontal silica tube from the furnace. The sample was analyzed by XRD (D8 ADVANCE BRUKER) and semi-quantitative analysis using RIR (Reference Intensity Ratio) method was conducted by PDXL2 software.

To clarify the reactivity between two oxides, 10 samples were prepared. Mixed samples of CaO+FeO, CaO+Fe₃O₄ and CaO+Fe₂O₃ was investigated to see the reactivity of CaO and Fe oxide mixture. Also, CaO was mixed with SiO₂ or Al₂O₃ to observe the reactivity between CaO and gangue minerals. To see the reactivity of FeO and gangue minerals, mixed samples of FeO+SiO₂, FeO+Al₂O₃ and FeO+MgO were prepared. Mixed samples of SiO₂+Al₂O₃ and MgO+Al₂O₃ were also investigated.

Additionally, mixed sample of CaO+FeO+SiO₂ was prepared to observe the reactivity between three oxides. Also, CaO+FeO+SiO₂+Al₂O₃ and CaO+FeO+SiO₂+MgO mixtures were investigated to clarify the effect of Al₂O₃ and MgO addition.

3. Results and Discussion

Figure 1 shows the XRD pattern of experiment using CaO and SiO₂. From CaO–SiO₂ binary phase diagram shown in Fig. 2, the equilibrium phases that exist at 1 373 K for the mixed ratio of present work are CaO·SiO₂ and 3CaO·SiO₂. However, CaO, SiO₂ and 2CaO·SiO₂ were observed after the experiment. From the fact that very stable 2CaO·SiO₂ compound exists in CaO–SiO₂ binary system, affinity between CaO and SiO₂ is large. However,
CaO+SiO$_2$ mixture will not be in equilibrium state after 1 hour heating at 1 373 K.

**Figure 3** shows the phase diagram of CaO–FeO and CaO–Fe$_2$O$_3$ binary system. When oxides were mixed at same weight ratio, equilibrium phase that exist at 1 373 K are CaO and 2CaO·Fe$_2$O$_3$. Liquid phase exists at 1 373 K in CaO–FeO phase diagram, while no liquid phase exist at the same temperature for CaO–Fe$_2$O$_3$ phase diagram. After mixed samples of CaO+FeO was heated at 1 373 K, sample was almost completely melted. Partial melting was observed for CaO+Fe$_2$O$_3$ mixture and no liquid phase was observed for CaO+Fe$_3$O$_4$ mixture. It was made clear that liquid formation of CaO and Fe oxide start at low temperature when Fe$_2$O$_3$ is reduced to FeO$_2$ and liquid phase increases when further reduced to FeO. The observed phase by XRD for CaO+FeO, CaO+Fe$_2$O$_3$ and CaO+Fe$_3$O$_4$ mixed samples are shown in **Fig. 4**. The phases observed after experiments were CaO and 2CaO·Fe$_2$O$_3$ and this agree with predicted phases at 1 373 K from phase diagram. Peaks for CaO+FeO mixture were weak due to existence of liquid phase. Also, Fe was detected in CaO+FeO and CaO+Fe$_3$O$_4$ mixed sample. It can be said that reactivity of CaO and Fe oxide is large. Reactivity between two oxides was investigated and it was summarized in **Table 1**. Also, the XRD patterns of experiment using CaO+Al$_2$O$_3$, FeO+SiO$_2$, FeO+Al$_2$O$_3$, FeO+MgO, SiO$_2$+Al$_2$O$_3$ and MgO+Al$_2$O$_3$ are shown in **Fig. 5**. Analysis by SEM-EDS was conducted for FeO+MgO mixture and it was confirmed that (Fe, Mg)O was present after the experiment. The reactivity of oxide mixtures that predicted phases agreed with observed phases was considered high. The reactivity of mixtures that didn’t match with predicted phase was considered as moderate. For the mixture of SiO$_2$ and Al$_2$O$_3$, oxide compound was not detected after experiment and the reactivity was low. Reactivity of Fe oxide and CaO tends to be high, while that of Al$_2$O$_3$ is low.

The XRD result for CaO+FeO+SiO$_2$ mixture is shown in **Fig. 6**. The phases observed were FeO, SiO$_2$ and 2CaO·SiO$_2$. It should be mentioned that CaO was likely to be dissolved into FeO phase. The predicted phases at 1 373 K for CaO–FeO–SiO$_2$ mixture was CaO·SiO$_2$ and CaO·FeO·SiO$_2$. It is clear that the phases present in the sample held at 1 373 K for 1 hour is completely different from the predicted phases from phase diagram. Also, 2CaO·Fe$_2$O$_3$ and FeO·SiO$_2$ phases that formed in the previous experi-
<table>
<thead>
<tr>
<th>Mixed oxides</th>
<th>Predicted equilibrium phases</th>
<th>Observed phases</th>
<th>Reactivity</th>
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<tr>
<td>CaO Fe₂O₃</td>
<td>CaO 2CaO · Fe₂O₃</td>
<td>CaO 2CaO · Fe₂O₃</td>
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</tr>
<tr>
<td>CaO Fe₃O₄</td>
<td>CaO 2CaO · Fe₂O₃</td>
<td>Fe</td>
<td>high</td>
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<tr>
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<td>CaO FeO</td>
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</tr>
<tr>
<td>CaO SiO₂</td>
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</tr>
<tr>
<td>CaO Al₂O₃</td>
<td>3CaO · Al₂O₃ 12CaO · 7Al₂O₃</td>
<td>CaO Al₂O₃ 3CaO · Al₂O₃</td>
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</tr>
<tr>
<td>FeO SiO₂</td>
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<tr>
<td>FeO Al₂O₃</td>
<td>FeO FeO · Al₂O₃</td>
<td>FeO FeO · Al₂O₃</td>
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<tr>
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<td>(Fe,Mg)O</td>
<td>(Fe,Mg)O</td>
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<tr>
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<tr>
<td>MgO Al₂O₃</td>
<td>MgO MgO · Al₂O₃</td>
<td>MgO MgO · Al₂O₃</td>
<td>moderate</td>
</tr>
</tbody>
</table>

Table 1. Reactivity between two oxides heated at 1 373 K under Ar.

Fig. 5. XRD results for CaO + Al₂O₃, FeO + SiO₂, FeO + Al₂O₃, FeO + MgO, SiO₂ + Al₂O₃ and MgO + Al₂O₃ mixture heated at 1 373 K under Ar for 1 hour.

ment for CaO + FeO and FeO + SiO₂ mixtures were not observed in the ternary oxide mixture. It can be said that the reactivity of CaO and SiO₂ to form 2CaO · SiO₂ is much higher than reactivity of CaO + FeO and FeO + SiO₂ and CaO completely reacted with SiO₂ in the present experiment.

The XRD results for CaO + FeO + SiO₂ + Al₂O₃ and CaO + FeO + SiO₂ + MgO mixtures are shown in Fig. 7. Semi-quantitative abundance ratio of phases observed after heating at 1 373 K for 1 hour for CaO + FeO + SiO₂, CaO + FeO + SiO₂ + Al₂O₃ and CaO + FeO + SiO₂ + MgO mixtures are shown in Fig. 8. The observed phases for CaO + FeO + SiO₂ + Al₂O₃ mixture were Fe₂O₃, 2CaO · SiO₂, 2FeO · Fe₂O₃, and CaO. Since it was found from the experiment using two oxides that reactivity of CaO is high, no CaO was found after heating and all CaO reacted with SiO₂ or Al₂O₃ to form 2CaO · SiO₂ or CaO · Al₂O₃ or dissolved into FeO phase. Also, FeO didn’t react with other oxides. The observed phases for CaO + FeO + SiO₂ + MgO mixture were SiO₂, 2CaO · SiO₂, (Fe,Mg)O, 2FeO · Fe₂O₃ and CaO. Unlike other samples, some CaO remained unreacted.

Recalling that by heating mixture of CaO + FeO, sample was nearly completely melted, it is highly possible that liquid CaO–FeO phase formed for CaO, FeO containing samples. To clarify the formation mechanism 2CaO · SiO₂, additional experiment was conducted. Sample prepared by mixing 0.4 g of CaO, 0.4 g of FeO and 0.2 g of SiO₂ was heated at 1 373 K for 1 hour under Ar flow. Size of SiO₂ powder was increased to 100 μm. The SEM image of the sample after heating is shown in Fig. 9. As seen from Fig. 9, it was confirmed that 2CaO · SiO₂ formed at the interface of CaO–FeO liquid phase and SiO₂ solid phase. This CaO–FeO liquid phase can react with SiO₂ and highly possible to
react with Al₂O₃ to form oxide compounds. Reaction can be expressed as Eqs. (1) to (3).

\[
\begin{align*}
\text{CaO(s)} &+ x\text{FeO(s)} \rightarrow \text{CaO} - x\text{FeO}(1) \quad \text{(1)} \\
2\text{CaO} - x\text{FeO}(1) + \text{SiO}_2(s) &\rightarrow 2\text{CaO} \cdot \text{SiO}_2(s) + x\text{FeO}(s) \quad \text{(2)} \\
\text{CaO} - x\text{FeO}(1) + \text{Al}_2\text{O}_3(s) &\rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3(s) + x\text{FeO}(s) \quad \text{(3)}
\end{align*}
\]

From these reactions, it can be explained that FeO did react with CaO to form liquid phase at the early stage and finally FeO was separated out by strong affinity of CaO with SiO₂ or Al₂O₃. However, for CaO+FeO+SiO₂+MgO mixtures, the experimental result can’t be explained by Eqs. (1) to (3). It is known that FeO and MgO forms solid solution. It is considered that FeO and MgO reacted rapidly to form (Fe,Mg)O solid solution. Unreacted amount of FeO was little, hence, CaO could not react with FeO to form CaO–FeO liquid phase. Recalling that by heating binary CaO+SiO₂ mixture, CaO, SiO₂ and 2CaO · SiO₂ formed, solid CaO and SiO₂ can react to from 2CaO · SiO₂. However, 2CaO · SiO₂ formation is accelerated by presence of CaO–FeO liquid phase. The intensity ratio for the primary peak of 2CaO · SiO₂ to SiO₂ can be obtained from Figs. 1 and 5 as 0.08 and 0.5 for CaO+SiO₂ and CaO+FeO+SiO₂ mixture, respectively. Also, it can be said that MgO can avoid formation of CaO–FeO liquid phase and retain the reaction of CaO with other oxides.

Fundamental reactivity between oxides at 1 373 K was investigated in the present work. It was found that the phases present in the sample after heating was different with equilibrium phases for most cases. The reactivity of CaO and FeO was found to be high and Al₂O₃ was low. Also, formation of CaO–FeO liquid phase will assist the reaction between CaO and other oxides. Addition of MgO will avoid CaO–FeO liquid formation. Information to control slag melting temperature was obtained in the present work.

4. Conclusions

Fundamental reactivity between oxides at 1 373 K under Ar atmosphere was investigated. The phases observed after experiment was different from predicted phase and deviated from equilibrium for most experiment. Reactivity of various oxides was investigated and it was found that reactivity of CaO and FeO was high and Al₂O₃ was low. Formation of CaO–FeO liquid phase was found when CaO and FeO coexisted and this liquid phase will assist the reaction between CaO and other oxides. Also, it was found that presence of MgO will avoid CaO–FeO liquid formation by rapid reaction to form (Fe,Mg)O solid solution. Important knowledge to control slag melting temperature in blast furnace was obtained in the present work.

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