Evaluation of Softening, Shrinking and Melting Reduction Behavior of Raw Materials for Blast Furnace

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To evaluate influences on the softening and melting behavior of blast furnace raw materials, the examinations of high temperature properties in various types of raw materials for blast furnaces were executed. Shrinking behavior before reaching approximately 1300°C is estimated by using softening viscosity taking into consideration pores of particles, and void ratio as well as liquid phase ratio of the layer. The softening viscosity of the solid phase of approximately 10¹⁰ Pa·s was obtained and the influence of the mineral species of the solid phase or temperature is small. Melting reduction sharply progresses through expanding the liquid phase deriving from FeO and gangue. And this behavior is affected with position of the reduction curve and the liquidus curve. Sinter forms a solid phase from FeO and gangue due to a rise of reduction degree according to melting reduction. This solid obstructs contact of the liquid phase including FeO with coke, which restricts the progress of melting reduction. On the other hand, with lumpy ore and pellet, melting reduction rapidly progresses without interruption, since no solid phase is formed even when FeO decreases due to melting reduction.

KEY WORDS: blast furnace; softening–melting; high temperature properties; softening viscosity; melting reduction.

1. Introduction

A cohesive layer was identified as a dominant factor in blast furnace operation from the results of studies on dissection of blast furnaces.1) And the significance of effects on the operational performance of a blast furnace has become obvious according to subsequent studies. Many researches have also been achieved on softening and melting behaviors of sinter, pellet, lump ore and other raw materials for a blast furnace as one of the dominant factors of cohesive layer formation. And testing methods for high temperature properties’ estimation of blast furnace burden materials have been developed and thus are now extensively diffused and actively exploited.2–4)

However, while various indexes4,5) are presented regarding elucidation of the relation between the softening and melting behavior of respective raw materials for a blast furnace and operation result of blast furnaces, no satisfactory knowledge has been acquired concerning the effect of diverse factors such as composition and reduction behavior affecting the softening and melting behavior of raw materials for a blast furnace. In particular, concerning shrinking behavior, while many trials5–8) have been conducted to organize data according to softening viscosity, no synthetic evaluation of various blast furnace burden materials has been available. One reason for this seems that raw materials for a blast furnace have a composite structure comprising plural minerals. In addition, handling this problem becomes further compounded by the necessity of consideration of a packed bed structure comprising voids and porous particles, which varies with reaction and phase changes. These factors compel us to evaluate the effects of raw materials for a blast furnace on operation result of blast furnaces through an examination under actual operation.

In the present study, in order to evaluate dominant factors in high temperature properties’ behavior led by the softening and melting of raw materials for a blast furnace, experiments and analysis were performed taking the above phenomenon into consideration. And the discussion based on those results was conducted.

2. Experimental Devices and Conditions

Samples for experiments were sinter, acid pellet, self fluxed pellet, and Brazilian lumpy ore in actual use for blast furnaces. The composition of samples is shown in Table 1. Samples are 10–15 mm in diameter.

A measuring device for high temperature properties was shown in Fig. 1.4) A sample having a layer thickness of 70 mm was charged in a crucible and coke of 10–15 mm in diameter with a layer thickness of 20 mm was placed over and below that. Subject to the condition of constant layer thickness, the charge of a sample weighed differently.

Experimental conditions are shown in Fig. 2. Heating up rate is 10°C/min below 1000°C and 5°C/min from 1000°C to 1550°C, and then each experiment is finished. Gas flow is 34.0 NL/min of N₂ below 800°C and the same flow rate of reducing gas from 800°C to 1550°C. And composition of the reducing gas is CO:H₂:N₂ = 29.4:3.5:67.1 (%). The load
of 0.1 MPa is added over 800°C. Behavior of softening, shrinking and reduction was evaluated through measuring variations in layer thickness, gas composition and pressure drop.

3. Experimental Results and Considerations

3.1. Experimental Results

The results on the high temperature properties of the respective raw materials and the indexes obtained from the experiments are shown in Figs. 3–6 and Table 2, respectively. Hereupon, $T_{200}$ is the temperature at which the pressure drop of a sample has reached 200×9.8 Pa as it rises, $T_{200}$ is the temperature at which the pressure drop has reached 200×9.8 Pa again as it falls, $T_d$ is the temperature at which dripping starts, $R_{1000}$ is the reduction degree at 1 000°C, and $R_{1200}$ is the reduction degree at 1 200°C. In addition, the reduction degree is estimated from changes in gas composition on hematite basis. In all samples it is common that raw

<table>
<thead>
<tr>
<th>Sample</th>
<th>T.Fe (mass%)</th>
<th>FeO (mass%)</th>
<th>CaO (mass%)</th>
<th>SiO₂ (mass%)</th>
<th>Al₂O₃ (mass%)</th>
<th>MgO (mass%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sinter</td>
<td>57.81</td>
<td>7.02</td>
<td>10.12</td>
<td>4.89</td>
<td>1.89</td>
<td>0.64</td>
<td>35.8</td>
</tr>
<tr>
<td>Acid Pellet</td>
<td>67.29</td>
<td>–</td>
<td>0.71</td>
<td>2.00</td>
<td>0.30</td>
<td>0.39</td>
<td>26.3</td>
</tr>
<tr>
<td>Self Fluxed Pellet</td>
<td>65.70</td>
<td>0.57</td>
<td>2.61</td>
<td>2.28</td>
<td>0.62</td>
<td>0.06</td>
<td>24.3</td>
</tr>
<tr>
<td>Lumpy Ore</td>
<td>67.46</td>
<td>0.38</td>
<td>0.03</td>
<td>1.29</td>
<td>0.89</td>
<td>0.02</td>
<td>13.4</td>
</tr>
</tbody>
</table>
materials start shrinking once temperature surpasses approximately 1000°C, then, the layer thickness diminishes at a nearly constant speed as the temperature rises. Shrinking rate reduces once with conspicuous pressure drop increases, however it tends to rise again just before dripping.

3.2. Evaluation of Shrinking Behavior According to Softening Viscosity

Evaluation of shrinking behavior according to softening viscosity was attempted as in the previous studies.\(^3\),\(^6\)--\(^8\)

The apparent softening viscosity is a value representing the shrinking resistance of an overall packed bed, and is defined in Eq. (1),

\[
\frac{1}{L} \frac{dL}{dt} = -P/\eta
\]

where, \(L\): layer thickness (m), \(P\): load (Pa), \(t\): time(s), and \(\eta\): apparent softening viscosity (Pa·s).

The apparent softening viscosity calculated from the experimental results is shown in Fig. 7. Any value of the samples tends to indicate around 10\(^9\) Pa·s till shrinking starts, and sharply decreases once after shrinking starts, then, gradually diminishes to the vicinity of dripping, and sharply decreases again just before dripping.

However, when compared with the results\(^6\) measured by Fukami et al. which were showed in the same figure with thin lines, values are generally low and the most remarkable point has a small value around 1/1000. The apparent softening viscosity \(\eta\) evaluated hereupon includes the effect of structural factors such as pores and voids contained in particles and packed beds, and the effect of the formed liquid phase. These effects weaken the strength of solid structure. So it is considered that values evaluated hereupon became smaller than those of the compact solid phase used in the experiment by Fukami et al.

So to eliminate these effects, it is postulated that the effects of pores and voids affecting softening viscosity may be handled similarly to various elastic properties of solid such as Young modulus. Thus, the following relation holds\(^9\) whereby the apparent softening viscosity depends upon the cubic volume fraction of the solid phase.

\[
\eta = \eta_0 V^3
\]

where, \(\eta_0\): softening viscosity (Pa·s) of solid phase, \(V\): volume fraction of solid phase (–).

Moreover, it is postulated that only the solid phase affects softening viscosity, and that it is impossible for the liquid phase to resist shrinking under the condition free of obstructing its fluidity with rich pores and voids.

Volume fraction of solid phase was evaluated as follows. The composition at each point of time was estimated based on reduction degree and the initial composition and weight. It was postulated that as for reduction process of iron oxide, Fe\(_2\)O\(_3\) is completely reduced into Fe\(_3\)O\(_4\) first, then, Fe\(_3\)O\(_4\) into FeO, and FeO into Fe, step by step. This assumption allows a given reduction degree to uniquely determine the mode of iron and iron oxide. And temperature and pressure of the whole system were known as experimental condition. Thus with the assumption that melting behavior was ruled by the thermodynamic equilibrium of CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–MgO–FeO system, the quantity and composition of the solid phase can be evaluated by thermodynamic calculation. And those of the liquid phase are also evaluated as the rest. Here the values were evaluated by SOLGASMIX\(^{10}\) using a cell model. And in evaluation, it is considered various phases, not only monoxide such as FeO, CaO, SiO\(_2\), Al\(_2\)O\(_3\) and MgO but also composite oxide such as 2FeO·SiO\(_2\), CaO·SiO\(_2\)·Al\(_2\)O\(_3\), 2CaO·MgO·2SiO\(_2\) and so on. In addition, it can be postulated that iron metal was considered wholly as a solid regardless of cementation under the coexistence of iron oxide.

In density estimation of liquid phase and solid phase to obtain volume, the effect of thermal expansion and phase transition was neglected because it is assumed to be insignificant. Moreover, as for the density of composite oxides such as fayalite, calcium silicate and multi-component calcium ferrite, it was postulated that additivity could be satisfied regarding respective constitutive compounds. Further-
more, the volume left after subtracting the liquid phase and solid phase was considered as for the gas phase.

The softening viscosity of the solid phase obtained through such correction is shown in Fig. 8. When compared with the results\(^6\) of Fukami et al., while the figure says that little dependency upon temperature was observed, the samples have similar values to that of the softening viscosity in the single mineral sample of reduced iron and FeO, around 1 200°C. This ensures that the handling is reasonable when it is considered that the samples contain iron metal and FeO as the primary solid phase in the vicinity of composition of the samples.

The reason why the behavior of the softening viscosity of the solid phase is similar to that of sponge iron than that of pig iron when the ratio of iron metal becomes higher is surmised as follows. Pig iron generates the liquid phase at a lower temperature significantly than pure iron due to the existence of carbon with cementation. And moreover, the volume fraction of the solid phase diminishes. Therefore, the apparent softening viscosity of pig iron seems to be lower than the softening viscosity of the solid phase. On the other hand, the sponge iron hardly generates the liquid phase before reaching the melting point (1 536°C), because it has little cementation in advance. Therefore, the apparent softening viscosity of sponge iron indicates nearly the same value as the softening viscosity of the solid phase.

Furthermore, separation of a solid phase softening viscosity into the respective components of solid phase was attempted, but failed to obtain any significant value. This may be caused by the fact that gangue is hardly regarded as a simple mixture of relevant oxides, since during reduction they exist as composite oxides such as fayalite with lumpy ore and multi-component calcium ferrite with sinter. And that difference of softening viscosity among components is too little to evaluate from these experimental results. How- ever, it is considered from the obtained results in the present study that shrinking behavior is more predominantly affected by the volume of the solid phase occupying a packed bed or the volume of pores, voids and liquid phase than by mineral species constituting particles and the temperature dependency of those.

Fig. 8. Softening viscosity of solid phase of samples excluding the effect of void and liquid phase. Thin lines (with *) are experimental results by Fukami et al.\(^6\) Solid lines are results of casting sample. Dotted lines are results of pressed powder sample.

Meanwhile, softening viscosity sharply falls in high temperature around 1 300°C. This seems because the effect hastening the apparent shrinking of the layer of the following factors cannot be taken into consideration.

(1) Formed liquid phase of high fluidity penetrates voids of the coke layer.

(2) The iron metal at the position in contact with coke melts by cementation, turns into liquid phase and penetrates the voids of the coke layer.

In particular, pellet and lumpy ore have remarkable decreases in softening viscosity till reaching a dripping temperature after surpassing 1 300°C. Transition in the volume fraction of iron metal in the solid phase is shown in Fig. 9. In this figure, quantity of iron metal was estimated by reduction degree of experimental results. And condition of iron metal was regarded as the solid phase in each sample. Quantity of other solid phase was estimated by thermodynamic calculation on CaO·SiO\(_2\)–Al\(_2\)O\(_3\)–MgO–FeO system of all gangue and remained FeO. The temperatures at which all gangue turns into the liquid phase with the solid phase of only iron metal are plotted with open keys, which are 1 327°C of lumpy ore, 1 318°C of acid pellet and 1 302°C of self fluxed pellet. Except sinter, these values are lower than experimental results of dripping start temperature \(T_d\) plotted with closed keys (or in Table 2). It seems that pushing molten gangue aside from between iron metal and coke by loads promotes the contact of the iron metal with coke and cementation. And the penetration of molten iron into the voids of the coke layer might advance with hastening apparent shrinking.

Meanwhile softening viscosity of sinter gradually decreases under a high temperature comparatively. It seems because 2CaO·SiO\(_2\) having a high melting point, i.e., 2 130°C or more with pure substances\(^1\) remains as a residue in the solid phase. This is actually verified from the analysis of the residues in the crucible after experiment. As shown in Fig. 9, iron metal occupies only 76% of the solid phase volume just before dripping, and the other 24% of solid phase is estimated as 2CaO·SiO\(_2\), which is considered to

Fig. 9. Calculation result of transition of volume fraction of metal in solid phase. Open keys are calculated temperatures at which all gangue turns into the liquid phase with the solid phase of only iron metal. Closed keys are dripping temperature in experimental results.
remain between iron metal and coke and to impede cementation. So it seems that the effect of the cementation of iron metal on shrinking was not so conspicuous.

3.3. Effect of Liquid Phase Rate Affecting Reduction Behavior

The transitional relation between the temperature of each sample and reduction degree is shown in Figs. 10–13. While reduction rate gradually decreases due to pore blockage caused by progress of reduction and shrinking, it is sharply accelerated around 1300°C. This is due to progress of melting reduction and is verified also from the conspicuous increase of CO in exhaust gas.

Hereupon, as described above, the liquid phase rate can be evaluated by thermodynamic calculation from reduction degree and temperature. Therefore, the temperature at which all FeO and the gangue turn into the liquid phase is also obtained for the given reduction degree. Or it means evaluation of the liquidus curve of FeO and gangue as function of reduction degree. This liquidus curve is also shown in Figs. 10–13 as each dotted line. And right ordinate is labeled with composition except iron metal of FeO.

These figures reveal that the reduction rate is rapidly accelerated with changing behavior as the reduction curve approaches the liquidus curve. This is understandable when interpreting this fact as melting reduction advanced with FeO turning into the liquid phase and thus was in contact with coke.

The temperature at which reduction behavior changed is slightly lower than the liquidus curve with self fluxed pellet and sinter. It is surmised that with self fluxed pellet and sinter, good fluidity of the generated liquid phase enabled melting reduction in contact with coke despite some of the solid phase remaining.

With lumpy ore and pellets in a region with a reduction degree of below around 90%, the liquid phase region indicated with the liquidus curve is extended to the region of high reduction degree. So once melting reduction starts, increase of the reduction degree doesn’t interrupt the progress of melting reduction. On the other hand, the liquid phase region indicated with the liquidus curve is extended to the region of low reduction degree with sinter. So it emerges that sinter forms a solid phase from FeO and gangue due to a rise of reduction degree according to melting reduction. It is considered that this solid obstructs contact of the liquid phase with the coke and subdue the progress of melting reduction till melting starts owing to rising temperature. Consequently, it is assumed that the melting reduction progressed along the liquidus curve of FeO and gangue.

This difference is qualitatively interpreted as follows. For simplicity, it is assumed that Al₂O₃ and MgO are equivalent to SiO₂ and CaO in weight respectively. So CaO/SiO₂ is equivalent to (CaO+MgO)/(SiO₂+Al₂O₃). Hereafter, to distinguish it is written as (CaO/SiO₂)*. Then the lumpy ore in Table 1 is evaluated as (CaO/SiO₂)* = 0.02, acid pellet as
\[(\text{CaO}/\text{SiO}_2)^* = 0.48, \text{self fluxed pellet as} (\text{CaO}/\text{SiO}_2)^* = 0.92, \text{and sinter as} (\text{CaO}/\text{SiO}_2)^* = 1.59, \text{respectively. As three component phase diagram of CaO–SiO}_2–\text{FeO shown in Fig. 14, lumpy ore proves that the primary crystal is FeO as composition except iron metal of FeO is 76% or more, i.e. a reduction degree is 94% or less with the sample of T.Fe = 67.46%. In addition, it can be read also that the melting point lowers with a decrease in FeO, i.e. with a rise in reduction degree. So increase of the reduction degree doesn’t interrupt the progress of melting reduction. Cases are in the same way with pellets. With acid pellet of T.Fe = 67.29%, composition except iron metal of FeO is 56% or more, i.e. a reduction degree is 96% or less. And with self fluxed pellet of T.Fe = 65.70%, in composition except iron metal of FeO is 45% or more, i.e. a reduction degree of 96% or less. Meanwhile with the sinter, the primary crystal is 2\text{CaO} \cdot \text{SiO}_2 as composition except iron metal of FeO is or less, i.e. a reduction degree over 56%. Moreover, it may be read that the melting point is heightened, as FeO decreases, i.e. the reduction degree rises. So the melting reduction progressed along the liquidus curve of FeO and gangue. Hereupon, sharp progress of melting reduction being an endothermic reaction might affect a local temperature drop leading to negative impacts such as heat fluctuation of the blast furnace. In addition, when reduction delay arises in the upper part of the furnace and melting reduction increases in the upper part of the furnace, it is considered in case of sinter that growth of melting reduction may affect restrainedly by formation of the solid phase from the liquid phase comprising FeO and gangue. However, it is considered in cases of lumpy ore or pellet that growth of melting reduction may cause directly promotion of a local temperature drop at the lower part of the blast furnace without restriction by formation of the solid phase.

4. Conclusion
To evaluate influences of blast furnace raw materials on the softening and melting and the shrinking behavior, high temperature properties in various types of raw materials for a blast furnace were measured and its results were analyzed. Obtained knowledge is as follows.
(1) Shrinking behavior before reaching approximately 1300°C is estimated by using softening viscosity taking into consideration pores of particles, and void ratio as well as liquid phase ratio of the layer.
(2) The softening viscosity of the solid phase of approximately 10^{10}\text{Pa·s} was obtained, which coincided with the value of single minerals according to the conventional reports, and the influence of the mineral species of the solid phase or temperature dependency is small.
(3) Melting reduction sharply advances through expanding the liquid phase deriving from FeO and gangue. This behavior is affected with position of the reduction curve and the liquidus curve. Sinter forms a solid phase from FeO and gangue due to a rise of reduction degree according to melting reduction. This solid obstructs contact of the liquid phase with the coke and subdues the progress of melting reduction till melting starts owing to rising temperature. On the other hand, with lumpy ore and pellet, melting reduction rapidly progresses without interruption, since no solid phase is formed even when FeO decreases due to melting reduction.

REFERENCES