CHANGE IN THE STRUCTURE AND PRESSURE DROP OF SINTERING BED WITH THE ADDITION OF FeO AS AGGLOMERATION AGENT[1]

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Abstract

Considering the remarkable growth of steel prodution, lower grade iron ore resources have been required to be extensively utilized. In addition, lowering of coke consumption in the sintering process is another demand from the viewpoints of energy FeO bearing materials, e. g., millscale and partially reduced iron are focused as a altenative agglomeration agents of coke. Fundamental study on changes in structure and pressure drop of the sintering bed was carried out using lab-scale differential type sintering simulator. In the experiment, Coke, Metallic iron, FeO and CaO particles and model mini-pellet (Alumina Cored pellet: ACP) made of alumina ball as a nuclei particle and fine mixture of CaO and Fe_2O_3 as adhering shell are used as raw materials. When using (ACP + Coke), pressure drop increased until ACP started to melt. Then, it decreased gradually. (ACP + Metallic iron) showed similar behavior to (ACP + Coke) at the first step but it increase again and showed a second peak. (ACP + FeO) did not show significant change in pressure drop and structure of the bed through melting process. In contrast, such changes were clearly observed in the case of CaO addition. These results shows that existing state of CaO component strongly affects the structural change of sintering bed

Key words: Sinter; Sintering simulator; FeO; Bed permeability; Existing state of CaO.

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1 INTRODUCTION

Price of the iron ore resources considerably rose in the 21st century.[1] One of the reasons is an increase in crude steel production in the world. Since the production will be increased, this price continues to rise for several years. Since the increase in the steel production accelerates a depletion of high quality iron ore resource.[2] steel industry becomes to use large amount of low quality iron ores in terms of gangue minerals, combined water and particle size distribution. Goethite ore which contains combined water is well known as of difficult for sintering. There have been many researches on sintering on such ores and a number of important results have been achieved. However, It is further necessary to develop the technologies for upgrading lower grade iron resource and its utilization.[3]

One of the methods to utilize goethite ore is not only as an iron source but also as an agglomeration agent in the sintering process after pre-reduction treatment.[4] In this method, goethite can be dehydrated and partially reduced to wustite by blast furnace gas, BFG of which CO/CO_2 is about 1. Wustite can be utilized for heat source because its oxidation reaction is exothermic. According to a sinter pot test by replacing half of coke to partially reduced ore, the melt formation and agglomerating of raw materials in the sintering bed have been observed. However, detailed mechanism of the behavior is not clear yet.

Some mill scale formed in rolling process also contains wustite, which is used in sintering process as iron sources. However, blending ratio of mill scale is limited because a large amount of mill scale addition will lead to a decrease in sinter productivity. Effective utilization of wustite bearing materials as agglomeration agent will make necessary coke addition less for the sintering process. This can directly relate to decrease in CO_2 emission in iron making process. However, studies on the reactivity of wustite/magnetite in the sintering bed have not been enough so far for understanding the effect on the structural change of the bed.

The purpose of this study is to study fundamentally examine the behavior of high temperature reaction of wustite in the sintering bed and its effect on the structural change of sintering bed. Especially, reactivity of wustite was compared with those of coke and metallic iron and the effect of CaO composition in the raw mixture on the melting behavior and structural change of the bed was evaluated.

2 EXPERIMENTAL PROCEDURE

The particles of wustite (ϕ 1.0 – 2.8 mm), coke (Fixed carbon 87.5 %, ϕ 1.0 – 2.0 mm) and metallic iron (ϕ 1.0 – 2.0 mm) were used as agglomeration agents. Wustite was made from reagent of hematite pellet (purity 99.9%, ϕ 2.0 – 5.0 mm) by reduction at 1000°C with $CO/CO_2 = 1$ atmosphere for 144 ks. Obtained wustite was identified by XRD and sieved to particle size 1.0 – 2.8 mm.

In order to eliminate the effect of shape and size of granule, gangue composition, and volume of formed melt in the sintering bed, model granules called as alumina cored pellet (ACP), which consisted of alumina balls (2 mmϕ) as nuclei and fine mixture of Fe_2O_3 and $CaCO_3$ as adhering layers, were used. They were prepared by using a disk pelletizer (60 mmϕ) with addition of water. Chemical composition of the adhering layer after calcination was shown in Table 1. The model pellets with several CaO compositions in afhering layer were prepared to control CaO level in the sample bed. Figure 1 shows chemical composition of the adhering layer on the phase diagram of $CaO-Fe_2O_3$ system. The particle size of model pellet was set between

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2.38 and 2.80 mm. In order to study the effect of exisence form of CaO, CaO particles with the particle size of 1.0 – 2.0 mm were prepared by calconation of $CaCO_3$ at 1400°C in air and crushed.

Table 1. Composition of the adhering layers of the model pellets

Sample name	FeO(%)	CaO (%)
ACP-15	85.4	14.6
ACP-25	73.9	26.1
ACP-35	61.2	38.8

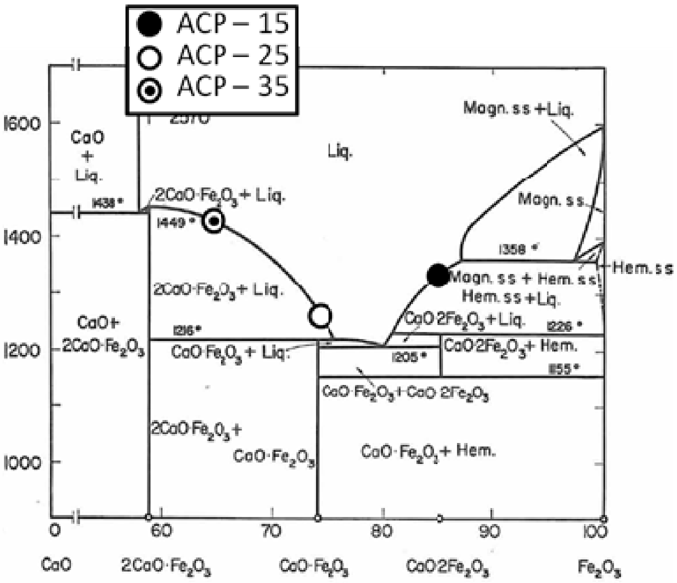

Figure 1. Composition of the adhering layers of the model pellets on the CaO - Fe_2O_3 phase diagram.

Sintering experiments were carried out by a sintering simulator shown in Figure 2.[5] Alumina tube with 35 mm in inside diameter was used as reaction tube. The height of sample bed was set at 20 mm. Packed beds of alumina balls (2 mmϕ) were placed at 50 mm above and 20 mm below the sample bed.

The wight of model pellet is 26g and hight of sample bed is 20 mm in coke case. As shown in Table 2, model pellet were chosen to keep CaO composition of sample bed 10 mass% in the case using metallic iron and wustite and 15% the case using coke. 5 mass% addition of coke as agglomeration agent (Fe – 0, 1.31g-coke) was base condition of mixing ratio in sample bed. In this case, all of agglomeration agents were thought to be reacted to CO_2 and amount of other agglomeration agents were set as heat equivalent to the case of coke addition (37.5 kJ). Metallic iron was 6.02 g and wustite was 21.2 g. In these case, same amount of heat would generate when all agglomeration agent reacts to Fe_2O_3. When the addition method of CaO was changed, wustite (21.2 g) was mixed with lime particle (LP, 2.3 g).

The upper and lower beds are for preheating the inlet gas and for prevention the drop-down of the fine materials, respectively. After packing sample and alumina balls to the reaction tube, they were heated up to the specified temperature under N_2 stream in order to prevent the oxidation of agglomeration agent. When bed-temperature reached to 900 ºC, the gas flow rate was controlled at 4.5×10^{-4} $Nm^3\cdot s^{-1}$. After gas flow became steady, the gas was changed to N_2–21%O_2 gas mixture. The heat was started to generate by the oxidation reaction of agglomeration agents mixed in the sample and gave temperature profile to the bed. The bed-temperature at the center of the sample bed, border-temperature between sample bed and lower alumina ball, concentration of CO, CO_2 and O_2 of outlet gas and pressure drop of beds were measured with time lapse.

The cross section of the sample bed after reaction was observed to discuss the behavior of the structure change of sample bed.

Table 2. Experimental conditions

	CaO source	Coke(g)	Metallic Iron (g)	Wustite (g)	Total CaO in sample bed (wt%)	Diameter of agglomeration agent (mm)	Sample bed height (mm)
Fe-0	ACP-15	1.31	0.0	0.0	15.0	1.0 – 2.0	20
Fe-100	ACP-25	0.0	6.06	0.0	10.0	1.0 – 2.0	20
W-100	ACP-35	0.0	0.0	21.1	9.5	1.0 – 2.4	30
W-100	LP-10	0.0	0.0	21.1	10.0	1.0 – 2.4	20

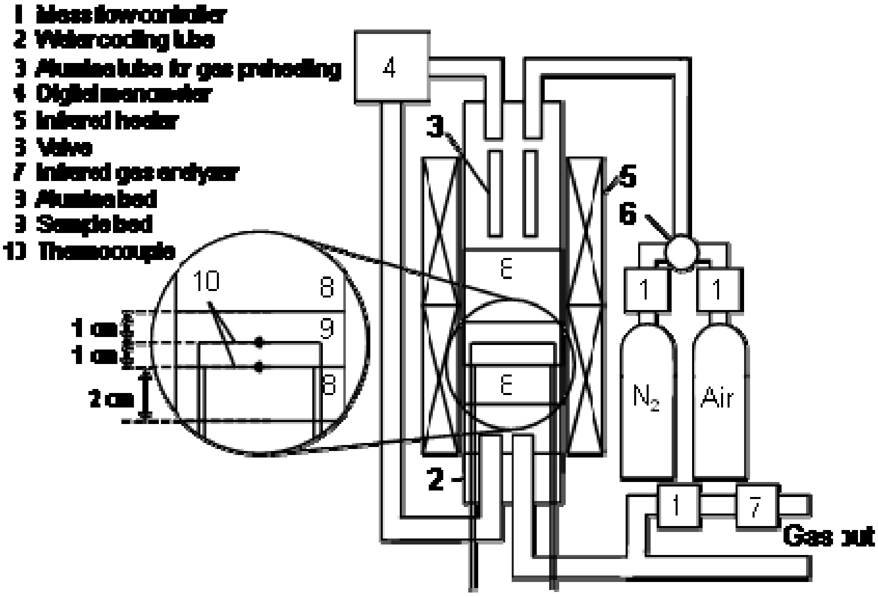

Figure 2. Schematic diagram of sintering simulator.

3 RESULTS AND DISCUSSION

Figure 3 shows changes in the temperatures of the sample bed and the border between sample and lower alumina beds with time for the cases of two types wustite (W - 100 ACP – 35, LP – 10), coke (Fe – 0 ACP - 15) and metallic iron (Fe – 100 ACP – 25). In each case, it increases rapidly and shows the peak value. Then, it decreases gradually. In the case using coke and metallic iron, bed temperature rises up to 1500 °C. However, in the case using wustite, it rises only up to 1200°C while the agglomeration agents are set as heat equivalent. In order to discuss this difference, the reaction ratios of each agglomeration agent were calculated by O_2 concentration in outlet gas. The change in calculated results with time is shown in Figure 4. The reaction ratio is defined as 1 when agglomeration agent reacted completely. Reaction ratio of coke is higher than that of other agglomeration agents and it reached to about 80% at 50 s. On the other hand, that of metallic iron is about 50 % while bed temperature using metallic iron is similar to that using coke according to Figure 3. This may be caused by the difference of heat transfer media between coke and metallic iron because the product of the latter is condensed phase. Using wustite and model pellet (W – 100 ACP – 35), reaction ratio at 50 s is 38 % which is four fifth that of metallic iron. Decreasing of reaction ratio causes a decrease in heat value, and it results in decreasing sample bed temperature. Further, it is one of key factors for decreasing temperature that the heat value per unit volume of the sample bed using the mixture of wustite and model pellet (W – a00 ACP - 35) was two thirds of that of others because this sample bed was 30 mm which was 1.5 times higher than that of other conditions. When the mixture of wustite and CaO particles (W – 100 LP - 10) was used, reaction ratio is 43 % at 50 s. It is 5 % higher than that for the case (W – 100 ACP – 35) and the peak temperature of the border is also higher as shown in Figure 3. In the reacted sample bed using metallic iron and wustite, metallic iron was not detected by chemical analysis. In the case of (Fe – 100 ACP – 25), therefore, it can be estimated that all of metallic iron added to the sample were changed to at least wustite and its heat value was calculated 25.7 kJ. On the other hand, the reaction of agglomeration agent of wustite means the change of Fe^{2+} to Fe^{3+}. Therefore, the heat values when using (W – 100 ACP - 35) and (W – 100 LP - 10) were calculated to be 21.1 and 23.9 kJ. The reason of these differences is thought to be caused by the reaction promotion of agglomeration reaction due to the melt formation which is discussed latter. Accordingly, CaO morphology such as the distribution and particle siza affects the reaction of agglomeration agent.

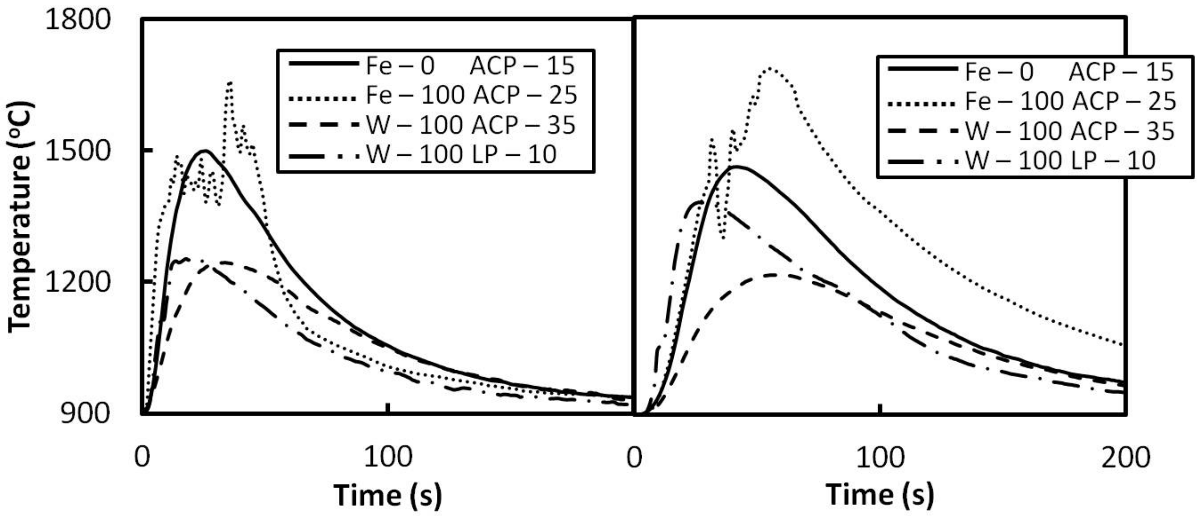

Figure 3. Change in temperature at the center of sample bed and the border between sample and lower alumina bed for the cases of coke breeze (Fe - 0), metallic iron (Fe - 100) and wustite (W - 100) used as agglomeration agent which was mixed with model pellet (ACP – 35) and lime particle (LP–10).

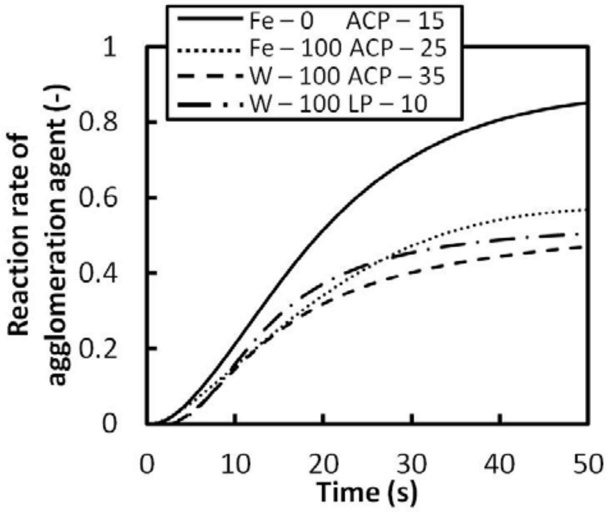

Figure 4. Change in reaction rates of the different agglomeration agents: coke breeze (Fe - 0), metallic iron (Fe - 100) and wustite (W - 100) which was mixed with model pellet (ACP – 35) and lime particle (LP – 10).

Figure 5 shows the change in the total pressure drop of the sample and alumina beds in the case using various agglomeration agents. In the case of coke (Fe – 0 ACP - 15), pressure drop once increases due to an increase in bed temperature by the reaction of agglomeration agent. After a few seconds, it starts to decrease rapidly because of increasing the void value by the gasfication of coke and moving the void in model pellet, and then, the slope is pressure drop change decreases gradually by a decrease in bed temperature.[6] In the case of metallic iron (Fe – 100 ACP - 25), the pressure drop shows a similar trend to that of (Fe – 0 ACP - 15) for about 15 s after starting the reaction. However, it starts to increase again and shows a second peak at about 60 s. Then, it gradually decreases again. When CaO composition of the bed was 15 % such as the case of (Fe – 100 ACP 35), it shows same behavior.[7]

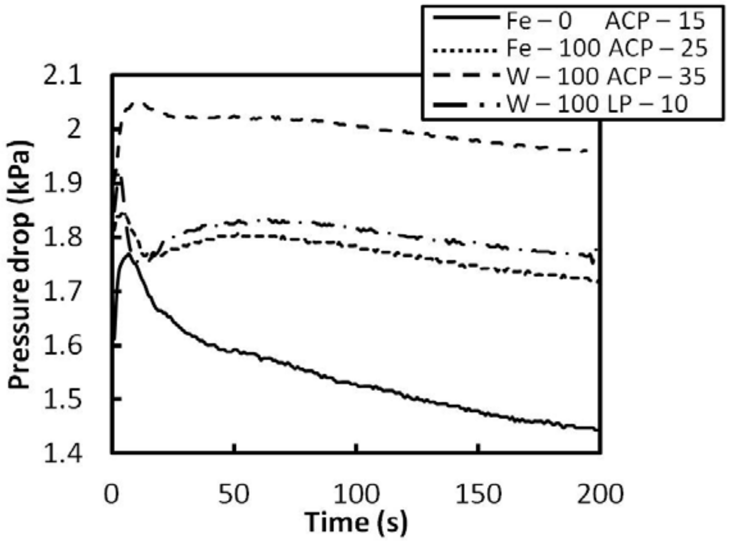

Figure 5. Change in pressure drop for the cases of coke breeze (Fe - 0), metallic iron (Fe - 100) and wustite (W - 100) used as agglomeration agent which was mixed with model pellet (ACP – 35) and lime particle (LP – 10).

In the case using the mixture of wustite and model pellet (W – 100 ACP – 35), pressure drop also increases rapidly simmilar to other cases. However, after that it shows only gradual decrease without showing rapid decrease and second peak. Using the mixture of wustite and CaO particle (W – 100 LP - 10), on the other hand, it shows simmilar behavior to that using metallic iron while a remarkable decrease appears at initial stage of reaction.

Figure 6 shows the vertical cross sections of sample beds after sintering. White spherial particle is alumina nuclei of pellet. In the case using metallic iron, number of alumina nuclei and amount of formed melt in the upper part of sample bed are less than that of the lower part. There is large amount of formed melt as blocks in lower layer. An increase in the amount of total iron used for the sample bed using metallic iron compared with the case using coke leads to increasing the amount of formed slag. It results in the flow down and localization of the melt to the lower part of the bed. Accordingly, most of pathes for air flow in the lower part of sample bed were caulked by the formed slag. Therefore, the pressure drop increased again as shown in Figure 5. In the case using wustite and model pellet (W – 100 ACP - 35), the materials which were observed as the particles did not melt and there is less structure change. Therefore, the pressure drop decrease by the structure change of the sample bed dose not occur and the change of pressure drop by temperature increase and decrease in the bed appeared. In the case using the mixture of wustite and CaO particle, on the other hand, the formation of melt was observed in the sample bed and the structure change appearred like that using metallic iron. Therefore, it shows simillar behavior to that of metallic iron.

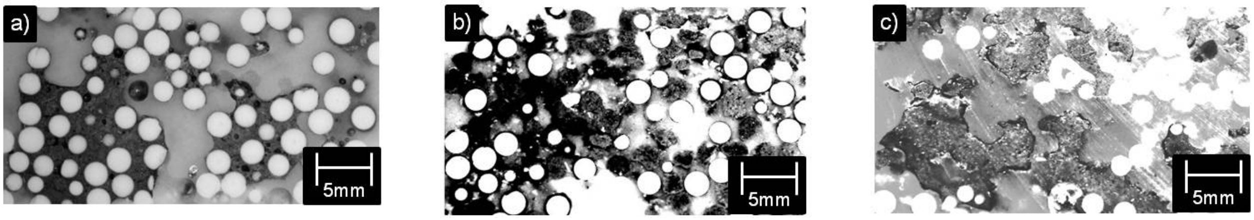

Figure 6. Vertical cross sections of the sample beds in the case using a) metallic iron (Fe-100 ACP - 25) and wustite b) (W – 100 ACP – 15) and c) (W – 100 LP – 10).

In order to discuss these differences caused by types of agglomeration agent and CaO morphology, the composition of the adhering layer of model granules and CaO on the phase diagram of $FeO-Fe_2O_3-CaO$ system[7] are shown in Figure7. The oxide melt forms by the reaction of adhering layer and CaO particle with iron oxide formed on the surface of the agglomeration agents with the certain compositions on the lines. In the case using metallic iron, FeO first forms on the surface of metallic iron when the oxidation reaction starts. The formed FeO melts because the bed temperature increased above 1400°C. The contact point of formed FeO and adhering layer can form the melt at 1200 °C. These suggest that the formation of large amount of melt leads to the flow down of the melt to the lower part and localization of the melt. In the case using wustite, Fe_3O_4 first forms on the surface of wustite when the oxidation reaction starts. In this case, the heat value was lower than that of metallic iron case and bed temperature did not reach up to 1300°C. Therefore the formed Fe_3O_4 on the surface of FeO and FeO itself do not melt. There is the only possibility that the melt forms at the contact point between magnetite and CaO source. When model pellets were used with FeO, the bed temperature as shown in Figure 3 did not reached to the lowest liquidus temperature crossed the chain line in Figure 7. As the bed temperature exceeds the solidus temerature, the melt will form. However, it amount is obviously smaller than that in the case above liquidas temperature. Therefore, a remarkable structure change would not occur as shown in Figure 6b). On the other hand, when using CaO particle, lowest liquidus temperature crossed the dashed line is below 1200°C. This suggests that large amount of melt forms at the contact point of CaO particles and agglomeration agents. According to Figures 6 and 4, in fact, the formation of molten oxide phase and high reactivility were confilmed from microstructure and reaction ratio, respectivley. It seems that difference of reactivility is caused by difference between diffusion velosity of solid and liquid phases. This melt leads to the structure change of the bed such as agglomeration and the following pressure drop change.

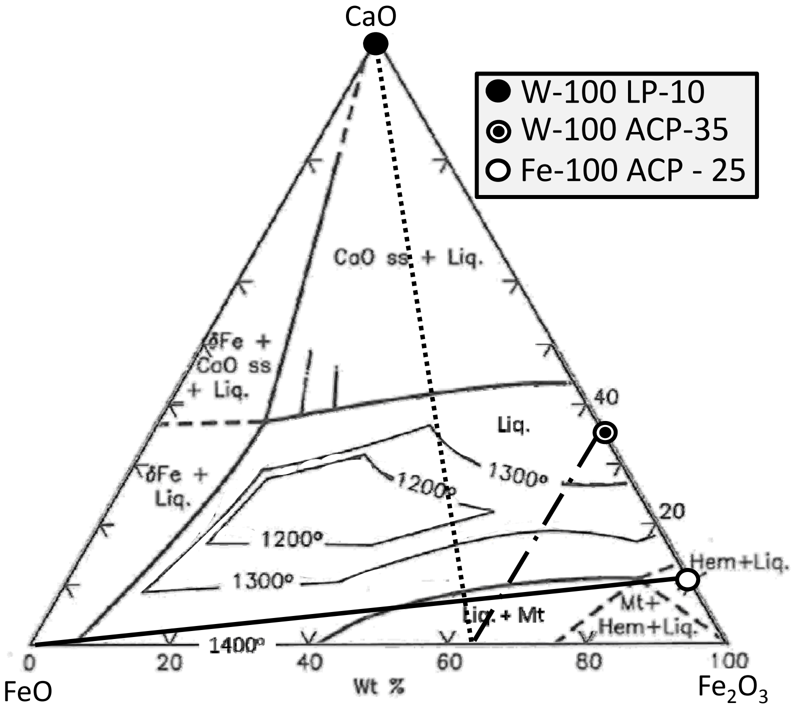

Figure 7. Composition of molten oxide phases on the phase diagram of FeO-Fe_2O_3-CaO system.[7]

These results suggest when only wustite was used as agglomeration agent without coke at the condition of equivalent heat value to that of coke, the amount of formed melt was not enough and pressure drop change was small. Reactivity of wustite is lower than that of metallic iron. The heat value is also smaller than the expected value. When CaO powder was previously mixed with iron oxide, this trend becomes significant. On the other hand, if CaO particles with a given size used without mixing, the melt forms easier than other case, and reactivity of agglomeration agent increases.

In previous study of replacement of the agglomeration agent from coke to wustite produced by partial reduction of iron ore pot test, maximum replacement ratio is 50% to obtain good sinter.[4]

This indicate that even in the case using wustite as agglomeration agent, sintering will be carried out with heat value and structure change being controlled by producing adequacy formed melt phase. The way of CaO addition and the effect of gangue in ore need more investigation.

The realization of optimum condition of the melt formation enable to produce the sinter controlled the heat generation and structure change.

4 CONCLUSIONS

A series of sintering experiment was carried out by using a sintering simulator. Behaviors of high temperature reaction of wustite in the sintering bed and its effect on the structual change of the sintering bed were fundamentally examined. Results are summarized as follows.

- When using wustite as an agglomeration agent, reactivity of agglomeration agent was lower than those of coke and metallic iron. Therefore, maximum bed temperature decreased considerably. In the case using model pellet prepared with insufficient CaO concentration, reactivity of wustite shows lowest value. In the case using CaO particles, which easily melt by the reaction with wustite, reactivety becomes higher than that of former case.
- The sample bed temperature of the mixture of wustite and model pellet did not exceed liquidus line corresponding to the local composition of CaO. Therefore, change in the pressure drop of the sintering bed occurs due to temperature change only because an amount of melt formation is not sufficient for the structural change of the sintering bed.
- On the other hand, the maximum bed temperature of the mixture of wustite and CaO particles exceeded 1200°C which is the lowest liquidus temperature of CaO – FeO – Fe_2O_3 ternary system. Therefore, the amount of formed melt was larger comparing to the case using model pellet and the pressure drop of the bed significantly decreased due to the structural change of the bed. It led to an increase in the bed permeability.

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