Note

Effect of Slag Components on Reducibility and Melt Formation of Iron Ore Sinter

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(Received on November 15, 2001; accepted in final form on January 23, 2002)

1. Introduction

Iron ore sinter is reduced only to the FeO stage until it reaches the thermal reserve zone of a blast furnace in iron-making process. Therefore, it is pointed out the reducibility of the sinter has a great importance at temperatures higher than 1 273 K.¹⁾ In particular, since the melting of slag in the cohesive zone of the blast furnace decreases the pore ratio of the sinter and prevents the gaseous reduction,²⁾ it is very important to promote the metallization ratio before the formation of the cohesive zone and to raise the softening temperature of the sinter. In the present work, the variation of temperature at which the melt formation begins with a fractional reduction is examined using three kinds of iron ore sinter and the effect of slag components on the melt formation is investigated. Carbon monoxide is generally used as a reducing gas in the study considering the reducibility of iron oxide in the blast furnace. On the other hand, the importance which considers the effect of H₂ gas on the reducibility also increases from the viewpoint of the control of CO₂ emission. In the present study, the reduction rate for each sinter is measured at 1 273 K using H₂–CO₂ mixtures and the effect of slag components on the reducibility of the sinter is also investigated.

2. Experimental

Three kinds of iron ore sinter are used in the present work and the chemical compositions are shown in **Table 1**. The contents of Al₂O₃ and MgO in the sinter are found almost the same and the effect of these components is considered negligibly small in the present work. Each sinter was crushed to the particle size of about 7 mm, of which the sample weighing 0.5 g was used for the following experiments.

Firstly, in order to know the reducible oxygen content of each sinter, the sample for each sinter was completely reduced with H₂ at 1 273 K as follows. The sample was put in an alumina crucible (38 mm O.D., 34 mm I.D., 45 mm height), which was set in a vertical SiC electric resistance furnace. After it was heated at 1 273 K in an argon, the sample was reduced by switching the ingoing gas to a hydrogen, which was blown onto the sample at a flow rate of 100 cm³/min(s.t.p.) for an hour. Then, the sample was with-

drawn from the furnace and was cooled in an argon. The reducible oxygen content was calculated from the weight change of the sample. For each kind of sinter, the experiment was carried out 12 times in order to confirm the reproducibility of the results. The determined reducible oxygen contents were statistically treated by calculating the 95 % confidence intervals of the average values. Subsequently, the samples, of which the fractional reductions from Fe₂O₃ range from 30 to 60 %, were prepared for each sinter as follows. The component of Fe₂O₃ in the sinter was reduced to FeO in an H₂–CO₂ gas mixture, of which the flow rates are 150 and 100 cm³/min(s.t.p.), respectively, for an hour at 1 273 K. The fractional reduction of the sinter sample reduced to FeO corresponds to about 30 % on the basis of the reducible oxygen content of Fe₂O₃. The sinter samples with higher fractional reductions were prepared by reducing for 15, 25, and 35 min in an H₂–CO₂ gas mixture, of which the flow rates are 200 and 100 cm³/min(s.t.p.), respectively, after they were pre-reduced to FeO under the conditions described above. The fractional reduction of the sample was calculated from the weight change of the sample. The experiments were conducted 6 times under the same conditions for each sinter. The 95 % confidence interval of the average value was calculated for each fractional reduction from the results.

The melt formation temperature was measured by DTA (differential thermal analysis) as follows. The samples, of which the fractional reductions from Fe₂O₃ are about 30, 45, and 60 %, were selected among all the reduced samples for each sinter and were crushed to the particle size of about 3 mm. The sample weight was about 50 mg. The fractional reductions, 30, 45, and 60 %, correspond to the metallization ratio of about 0, 21, and 43 % from the FeO stage, respectively. The DTA measurement was conducted at the heating rate of 10 K/min in an argon using a deep tray alumina pan (5.2 mm I.D., 5.1 mm height) at temperatures ranging from 1 273 to 1 573 K.

3. Results and Discussion

3.1. Reducibility of the Iron Ore Sinter

The reducible oxygen contents of three kinds of sinter are calculated from the weight change of the samples when they were reduced with H₂ at 1 273 K. The average values are 22.8(±0.4), 22.8(±0.4), and 21.7(±0.4) (mass%) for Sinter A, B, and C, respectively. The values in parenthesis show the 95 % confidence intervals of the average values. The 95 % confidence intervals are under 2 % of the average values and the derived values are considered to be reliable enough. Therefore, in calculating the fractional reduction, these derived values are used instead of the oxygen contents calculated from the chemical compositions shown in Table 1, in the present work. The variation of the fractional reduc-

Table 1. Chemical analysis of three kinds of iron ore sinter used in the present work.

Sample	(mass%)						
	T.Fe	FeO	CaO	SiO ₂	Al ₂ O ₃	MgO	CaO/SiO ₂
Sinter A	59.76	5.39	7.80	3.59	1.70	1.00	2.17
Sinter B	59.22	4.25	8.20	4.32	1.51	1.41	1.90
Sinter C	55.56	7.22	11.29	6.31	1.52	1.09	1.79

Fig. 1. Variation of the fractional reductions of Sinter A, B and C, which are pre-reduced to FeO, with time by H_2 - CO_2 reduction at 1273 K.

Table 2. Specific pore volume, specific surface area and mean pore diameter of sinter used in the present work.

Sample	Specific pore volume (m^3/kg)	Specific surface area (m^2/kg)	Mean pore diameter (μm)
Sinter A	3.23×10^{-5}	2.67×10^3	4.83×10^{-2}
Sinter B	3.76×10^{-5}	1.53×10^3	9.85×10^{-2}
Sinter C	2.30×10^{-5}	1.07×10^3	8.58×10^{-2}

tion with time by H_2 - CO_2 reduction at 1273 K is shown in Fig. 1 for each kind of sinter, which is pre-reduced to FeO. The fractional reduction shown in Fig. 1 is relative to the sample before the pre-reduction, *i.e.*, the fractional reduction at $t=0$ is about 30%. The 95% confidence intervals of the measured fractional reductions for each sinter are calculated about 4 to 8% of the average values. The fractional reductions for the sinter samples are regressed linearly against time using the least-squares method and the calculated lines are compared in Fig. 1. It is found that the reducibility of Sinter C is the worst of all the three kinds of sinter and Sinter B is the most reducible. The effect of lowering the SiO_2 content of the sinter on the properties at high temperature has been previously reported by several investigators.^{3,4)} It has been shown that as decreasing the SiO_2 content, the magnetite content of the sinter decreases and the reducibility of the sinter product is improved. Accordingly, one of the reasons of the higher reduction rates for Sinter A and B is considered to be the difference of the FeO (magnetite) content of the sinter. This would originate in the difference of the SiO_2 content of the raw materials for the sinter. The magnetite content is also considered to be controlled by other factors, such as the contents of other gangue minerals, the sintering temperature, and the cooling rate after the sintering. Specific pore volume, specific surface area and mean pore diameter of the three kinds of iron ore sinter are shown in Table 2. The specific pore volume is larger in the order of Sinter B, A and C. On the other hand, the specific surface area for Sinter A is larger than that for Sinter B. Accordingly, the smaller porosity abounds in Sinter A than in Sinter B. From these

Fig. 2. The DTA curves obtained for Sinter A with several fractional reductions at heating rate of 10 K/min.

Fig. 3. Dependence of the melt formation temperature on the fractional reduction for Sinter A, B and C.

information about the porosity of the sinter samples, the reduction rate is found to be positively correlated with the specific pore volume.

3.2. Melt Formation Temperature

The measured DTA curves of the pre-reduced Sinter A are shown in Fig. 2. Generally, the peak temperature of an exothermic or an endothermic reaction should be considered as the reaction temperature in the DTA measurements. However, in the case of the iron ore sinter, the endothermic reaction was observed over a wide temperature range and the peak of the DTA curve was not appeared clearly. Therefore, the temperature at which the gradient sign of the DTA curve changes to negative was decided to be the melt formation temperature in the present work, as shown in Fig. 2. The results of the DTA measurements for each sinter are summarized in Fig. 3, which shows the variation of the melt formation temperature with the fractional reduction of the sinter. From Fig. 3, it is found that the melt formation temperatures for Sinter A and B are higher than that for Sinter C and the melt formation temperature is raised as the reduction proceeds. In this respect, it is well known that the melting temperature of the slag in sinter is lowered by the dissolution of FeO during the reduction.²⁾ Accordingly, in the present work, it can be considered that the melt formation temperature is raised by decreasing the FeO (wustite) content of the sinter with the reduction progress. Regardless of the composition difference of the three kinds of sinter, the proportion of the temperature being raised with the reduction progress is almost the same among the sinter, *i.e.*,

the temperature for the sinter of 60% fractional reduction is about 50 K higher than that of 30% fractional reduction, of which the change corresponds to 43% metallization of wustite. The composition of molten slag at the melt formation temperature decided by the DTA measurement is considered as follows. The mean compositions of the three kinds of sinter, which are pre-reduced to FeO, are plotted on a CaO–SiO₂–FeO diagram^{5,6)} at 1423 K in Fig. 4. The formation of an eutectic melt, of which the composition is shown by an open square in Fig. 4, is expected at 1366 K. However, the eutectic melt can hardly form, in actual, because the composition is far from those of the three kinds of sinter and the solid line, which represents the coexistence of CaO·FeO·SiO₂ and FeO intercepts the two. Accordingly, from Fig. 4, the melt formation cannot be expected as long as the CaO·FeO·SiO₂ compound exists, namely under 1496 K. However, when the fact is taken into account that the plotted compositions are the mean values, the liquid which coexists with CaO·FeO·SiO₂ and FeO may form, as shown by in Fig. 4. Moreover, in actual, the melt formation is more complicated, because the other oxides, such as Al₂O₃ and MgO, have some effects on the phase diagram.

When the properties of the sinter are estimated at high temperature in view of the reducibility and the melt formation temperature, Sinter A and B are expected to be reduced sufficiently before the melt formation, because the reduction rate is faster and the melt formation temperature is higher than Sinter C. The melt formation is connected to the prevention of the gaseous reduction, *i.e.*, it can be considered that Sinter A and B have the better properties at high temperature and Sinter C has the worse. The gaseous reduction of Sinter C may be retarded because of the melt formation before it is reduced sufficiently. From the fact, in order to produce the sinter with the good properties at high temperature, it can be concluded that it is important to decrease the contents of SiO₂ and FeO under the higher CaO/SiO₂ ratio. The desirable condition on the chemical composition of the iron ore sinter to have good properties at high temperature is proposed by Hosotani *et al.*⁷⁾ and the summary is shown in Fig. 5. The sinter with the composition under the solid line in Fig. 5 is desirable to have good properties at high temperature. From Fig. 5, as the (mass% CaO)/(mass% SiO₂) ratio increases, it is requested to lower the SiO₂ content. It is found that Sinter A and B are in the region with the good properties, while Sinter C is out of the desirable region. The properties of the three kinds of sinter used in the present work can be also explained from this approach, in accordance with the results of the present work.

4. Conclusions

The three kinds of iron ore sinter, which are pre-reduced to FeO, have been reduced with an H₂–CO₂ gas mixture at 1273 K and the melt formation temperatures of the sinter with different fractional reductions have been measured. The following results are obtained:

(1) The reduction rate is faster and the melt formation temperature is higher for the sinter having lower FeO and SiO₂ contents. The melt formation temperature has a tendency to be raised as the CaO/SiO₂ ratio increases.

Fig. 4. Iso-thermal section of a phase diagram of CaO–SiO₂–FeO system at 1423 K.

Fig. 5. Desirable or undesirable region of iron ore sinter from the relationship between (mass% CaO)/(mass% SiO₂) and SiO₂ in sinter.

(2) The melt formation temperature of the sinter is raised as the reduction proceeds, because the FeO content of the sinter decreases with the reduction progress. The melt formation temperature for the sinter of 60% fractional reduction is about 50 K higher than that of 30% fractional reduction.

(3) When the properties of the sinter are evaluated in view of the reducibility and the melt formation temperature, it is important to decrease the SiO₂ and FeO contents under the higher CaO/SiO₂ ratio.

Acknowledgment

The authors wish to thank Mr. M. Nakamoto, Graduate Student of Osaka University, for his help in preparing this manuscript.

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