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Effects of Porosity and Slag Former Amount on Rate of Heating-up Reduction of Self-fluxed Pellet.

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Abstract

Six kinds of self-fluxed pellets were used in heating-up reduction experiments. It was found that the reducibility of pellet increased with the increase of porosity, increase of CaO/SiO_2, and decrease of slag former amount. Starting temperature of slag flowing-out decreased with increase of slag former amount and sintering temperature and increased with the increase of porosity. If the original characteristics of pellets (porosity, sintering temperature and slag former amount) are known, then starting temperature of slag flowing-out can be calculated under certain experimental conditions. It was also found that the shrinkage was controlled by the reduction rate at high temperature over 1000°C.

1. Introduction

In regard with blast furnace operation, the reducibility of iron ore is an important parameter which influences its efficiency and operating processes. On the other hand, the reduction of iron ore is affected by a lot of factors related to its chemical composition, physical properties, and micro structural aspects.

Many investigations have recently been made to reveal the factors influencing the reduction of iron ore. Some of these factors related to chemical composition of iron ore, which included SiO_2 content[1-5], CaO content[1,3,6], MgO content[3-4,6], Al_2O_3 content[2,7-8], and potassium content[3,9-12]. Effects of sulphur content in the reducing gas[13-14], and particle size of iron ore[15] have also been studied.

In this study, heating-up reduction under load experiments were carried out using six kinds of self-fluxed pellets and CO/N_2 mixture as reducing gas. The effects of porosity, sintering temperature, slag former amount (sum of weight percent of CaO, SiO_2, Al_2O_3, and MgO), and basicity (CaO/SiO_2) on reducibility of pellet and its behaviour in high temperature region were studied.

2. Method and materials

A scheme of experimental apparatus used in this study is shown in Fig. 1. The furnace used was a vertical one equipped with six SiC heating elements and an alumina reaction tube

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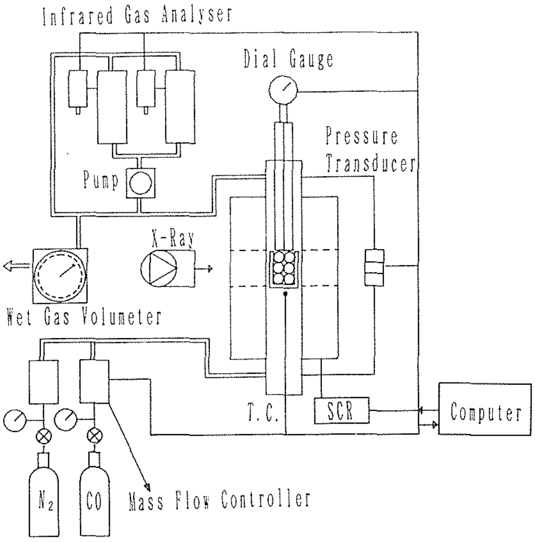

Fig. 1 A scheme of experimental apparatus.

(42 mm I. D. and 1000 mm L.) and controlled by a SCR power regulator. Taking X-ray pictures and also recording of video tape of samples were made in the course of reduction experiment using X-ray system. The reducing gas was prepared by mixing each component gas whose flow rate was precisely controlled by the thermal mass flow controller (MFC). CO and CO_2 contents of the outlet gas were analysed using the respective infrared gas analysers. The total flow rate of outlet gas was measured by a wet gas volumeter. A constant load of 1 kgf/cm^2 which adjusted by steel balls was applied on the samples in all experiments. The expansion and shrinkage of the samples was detected by an electrical dial gauge as the displacement of a silica rod setting to the top of sample bed. The pressure drop between the inlet and outlet gas was also continuously measured using a pressure transducer. All data from thermocouples, dial gauge, pressure transducer, wet gas volumeter, and infrared gas analysers were sampled by a micro computer.

Fig. 2 shows a scheme of graphite crucible in which six pellets of almost same size (11.2-11.5 mm in diameter) were placed on the top of coke layers supported by two graphite side plates. A coke plate (20×10 mm) was trimmed off and placed on the top of pellet column for uniform loading. Thus, the pellets were surrounded by carbonaceous materials. The uniform flow of reducing gas was also made possible

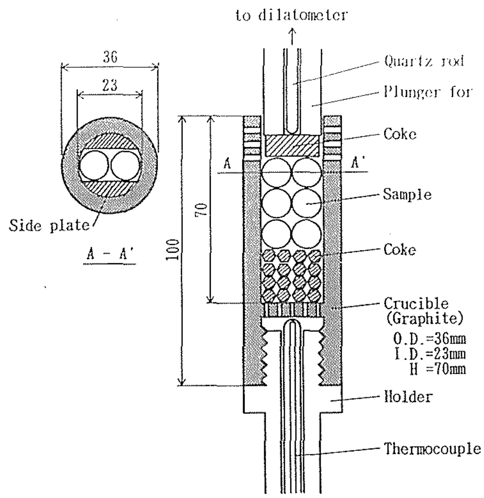

Fig. 2 Graphite crucible assembly.

through 72 holes of 0.8 mm in diameter at the bottom of the graphite crucible.

In all heating-up reduction experiments under load, the samples were heated in a nitrogen atmosphere up to 200°C from which the nitrogen was changed to reducing gas of a given flow rate and composition. Heating-up was started with the rate of 10°C/min and continued up to melting-down of the pellets. Total flowrate of reaction gas was 2000cm^3/min (STP) and the composition was 30vol%CO and 70vol%N_2 (table 1).

Table 1 Experimental conditions.

Cas composition	30 vol% CO-70 vol% N_2
Gas flow rate	2000 Ncc/min
Heating rate	10 °C/min
Load	1 kgf/cm^2
Temperature range	200 °C-melting-down

The rate of reduction (RDR) was calculated from the mass balance of oxygen of the inlet and outlet gas according to Eq. (1).

$$RDR(\%\ min^{-1})=[(CO+2CO_2)_{out}-(CO+2CO_2)_{in}].1600/22414/[O] \quad (1)$$

Where [O] is the amount of reducible oxygen (g) in six pellets. CO and CO_2 represent the mass flow rate of respective gas, which were analysed by infrared gas analysers. The reduction degree (TRD) at each time was also calculated by summation of RDR from the beginning of reduction expressed as Eq. (2).

$$TRD=\Sigma RDR.\ \Delta t \quad (2)$$

The ores used in this study were six kinds of self-fluxed pellets. The chemical composition and physical properties of pellets are given in table 2. In order to have specified porosities, each type of pellets was sintered at a different temperature. The samples B-a, B-b, and B-c had the same chemical compositions and slag former amounts and different porosities. The pellets A, B-b, and D were at the almost same porosities and basicities but different slag former amounts. The porosity and the slag former amount of types C and D were almost equal and basicity was different.

Table 2 Chemical composition and physical properties of self-fluxed pellets.

Sample		Chemical composition (wt. %)						Slag former amount (wt. %)	CaO/SiO_2 (−)	Sintering temp. (°C)	Porosity (%)
		T. Fe	FeO	SiO_2	Al_2O_3	CaO	MgO				
A		63.99	0.33	2.38	0.86	3.36	1.06	7.66	1.41	1220	24.30
B	a	59.60	2.17	4.21	1.76	5.85	2.13	13.95	1.39	1300	20.92
	b									1265	25.60
	c									1250	26.02
C		55.86	2.40	6.26	2.44	7.97	3.23	19.90	1.27	1265	24.96
D		54.89	0.54	6.25	2.34	8.66	2.67	19.92	1.39	1294	25.28

※Slag former amount : $SiO_2+Al_2O_3+CaO+MgO$

3. Results and discussion

Reduction rate (RDR) of pellet was calculated in the course of heating-up reduction by oxygen balance based on flow rates of CO and CO_2 of inlet and outlet. The reduction degree (TRD) was also calculated at each time by summation of RDR from the beginning of reduction. The curves of reduction degree (TRD) of all six kinds of pellets are plotted against temperature and shown in Fig. 3. Generally, whole reduction process may roughly be classified into two regions of

a) gas-solid reaction period in low temperatures and
b) gas-solid-liquid reaction period in high temperature.

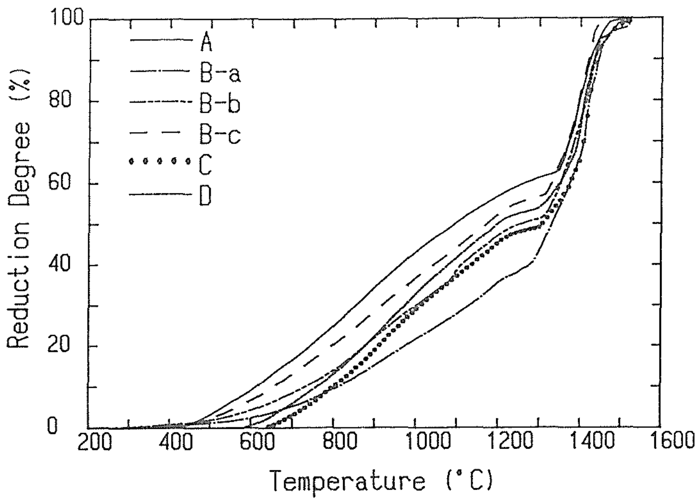

Fig. 3 Reduction curves of six kinds of pellets.

The region (a) is less than 1000°C and the slope of curve(or the rate of reduction) increases continuously. Then the region (b) is a part above 1000°C and the slope of TRD curve gradually decreases, which is caused from the closing of pore by formation of liquid slag inside the pellet.

In the first region (a), the reducibility of pellets can be compared among different kinds of pellets. In comparison with B-a, B-b, and B-c, which are of the same chemical composition and different porosity, the reducibility of pellet increases with increasing of porosity. Sample B-a of the lowest porosity has the lowest reducibility in all studied pellets. Comparing pellets A, B-b, and D, which are almost of the same porosity and basicity and different slag former amount, sample A of the lowest slag former amount and the highest hematite content has the highest reducibility among the all six kinds of pellets. Pellets C and D have the same slag former amount and porosity and different basicity (CaO/SiO_2). From TRD curves of these two kinds of samples, basicity also shows a positive effect on reducibility of pellet, when the basicity increases from 1.27 in pellet C to 1.39 in pellet D.

In high temperature region (b), there is a reduction retardation period in all cases at the beginning of the region, which is related to sintering of metallic shell at the surface and formation of melt inside the pellet. The reduction retardation period is followed by considerable rising of reduction degree and pressure drop due to start of smelting reduction after flowing-out of molten FeO-slag. It has been reported that the beginning of the cohesive zone in blast furnace would be due to this flowing-out phenomenon.

Starting temperature of reduction retardation and smelting reduction and also beginning of melting-down of pellet, which determine its high temperature properties, depend on its original characteristics and will be discussed later.

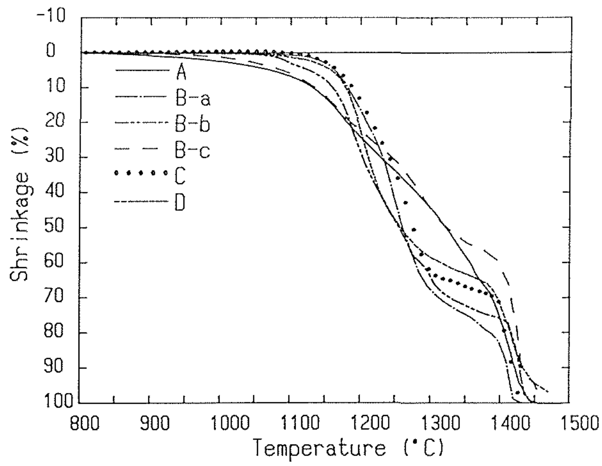

Fig. 4 Variations of shrinkage of pellets during heating-up.

Fig. 4 shows the diagrams of shrinkage of the bed of pellets in the course of heating-up reduction at a heating rate of 10 °C/min for all six kinds of pellets. An initial slight expansion of samples was observed, which turned to the shrinkage as the heating-up and reduction proceeded. There was an abrupt shrinkage before 1200 °C due to formation of molten slag within the pellets. In the other words, shrinkage was fast during reduction retardation period. Flowing-out of molten primary slag from about 1300 °C, at the end of reduction retardation period, was accompanied by slow shrinking of the samples. Finally, another abrupt shrinkage was observed over 1400 °C because of melting-down of metallic iron. Comparing the shrinkage diagrams of samples B-a, B-b, and B-c, the temperature at which contraction of the bed starts decreases by increase of porosity. It is noticeable that higher porosity of pellet led to higher reduction degree. It is also found from Fig. 3 that higher porosity results in

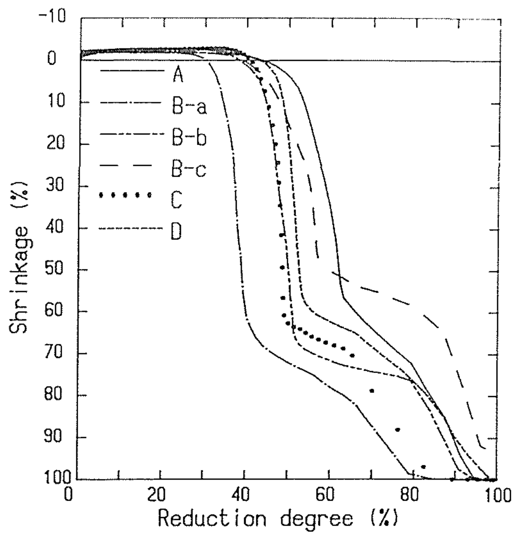

Fig. 5 Shrinkage vs reduction degree of pellets.

lower shrinkage starting temperature. From these facts, it is considered that the reduction degree is one of the shrinkage controlling factors at high temperature region. That is more clear in Fig. 5 in which shrinkage of samples is plotted against TRD. In the first abrupt shrinkage region, the slope of the curves is almost the same, that is, the ratio of shrinkage rate to reduction rate is almost same. So in that temperature region, over 1000 °C, it is considered that the shrinkage is controlled by reduction process.

Above mentioned high temperature (over 1000 °C) properties of pellet can be classified into four characteristic temperatures as follows:

1) temperature at which shrinkage starts (expansion changes to shrinkage)
2) temperature at which formation of melt starts
3) starting temperature of flowing-out of molten slag
4) starting temperature of melting-down of metallic iron

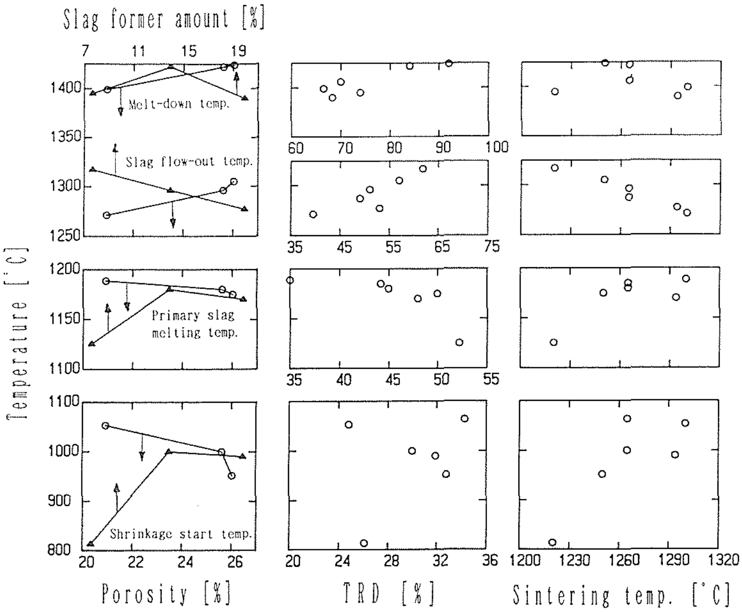

Fig. 6 Effects of slag former amount, sintering temperature, porosity, and TRD on high temperature properties.

Fig. 6 shows the effects of porosity, slag former amount, sintering temperature, and reduction degree (TRD) on these high temperature properties of pellet. Based on Fig. 3 and Fig. 6, the melting temperature of primary slag is affected by reduction degree which is related to porosity and slag former amount. Samples A and B-a of the highest and lowest reducibility had the lowest and the highest melting temperature of primary slag, respectively. The total reduction degrees at this temperature were the highest (52.2%) and the lowest (35%) among all six kinds of pellets for A and B-a, respectively. This temperature also increases by increase of the temperature at which the sample was sintered during preparation process.

The temperature at which flowing-out of slag occurs depends on porosity, slag former amount, sintering temperature and reducibility of pellet. This temperature increases with the increase of porosity and decreases by increasing of slag former amount and sintering temperature. Because, the pellet of higher porosity has more capacity for holding of molten slag and larger pores keeps the molten slag from flowing-out at lower temperature. Moreover, the thicker metallic shell at the surface of pellet, in the case of higher reducibility due to higher porosity, resists against flowing-out of molten slag and causes to an increase of this temperature. Therefore at a constant heating rate and composition of reducing gas, starting temperature of slag flowing-out may be considered as a function of porosity, slag former amount and sintering temperature. The amount of smelting reduction decreases with increase of starting temperature of slag flowing-out (T_f) and increase of reducibility of pellet (Fig. 3) which is desirable in blast furnace operation. In pellet A of the highest reducibility and the highest T_f, only 38% of reducible oxygen was removed through smelting reduction. While, in pellet B-a, of the lowest reducibility and the lowest T_f, 66% of reducible oxygen was reduced in smelting reduction process.

From these results, it was found that the starting temperature of slag flowing-out T_f is a function of slag former amount SFA, sintering temperature Ts and porosity ε. Using a multiple regression analysis method, Eq. 3 was found for calculation of T_f (starting temperature of slag flowing-out).

$$T_f = f(SFA, Ts, \varepsilon)$$

$$T_f = -131.3(SFA) - 0.362(Ts) + 287.2(\varepsilon) + 1699.6 \quad (3)$$

Where :

Variables

T_f : starting temperature of slag flow-out (°C)

SFA: slag former amount in pellet (−)

$SFA = (\%SiO_2 + \%CaO + \%Al_2O_3 + \%MgO)/100$

Ts : sintering temperature of pellet (°C)

ε : initial porosity of pellet (−)

Conditions

Reducing gas : N_2-30vol%CO

CaO/SiO_2 of pellet : 1.4 (-)

Heating rate : 10 (°C/min)

T_f is recalculated form Eq. 3 and compared with experimental data in Fig. 7 for all six kinds of pellet. There is a good agreement between calculation and experiment. In order to check the accuracy of this model, experimental results of previous studies performed by other researchers were compared with calculation from present model in table 3. In those studies, the experimental conditions and CaO/SiO_2 of pellet were the same as present work.

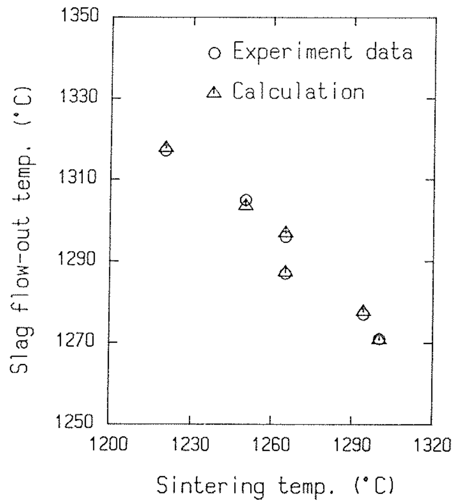

Fig. 7 Comparison between experiment data and model calculation.

Table 3 Comparison between previous studies and model calculation of T_f.

Previous work	Experimental data	Calculation data
Kondo et al. *	1308 °C	1314.2 °C
Takahashi **	1312 °C	1302.4 °C

* S. Kondo, K. Ishii, and Y. Kashiwaya
** N. Takahashi : private communication

4. Conclusion

Reducibility of iron ore and its high temperature behaviour are affected by its original characteristics and have an important influence on blast furnace operation. Using six kinds of self-fluxed pellets, heating-up reduction experiments were performed. The relationships between reducibility and high temperature properties of pellet were studied. Results obtained are as follows :

(1) The reducibility of pellet was affected by its original characteristics and increased with the increase of porosity and the decrease of slag former amount. Also in the case of constant porosity and slag former amount, reducibility increased as the basicity increased from 1.27 to 1.39.

(2) Starting temperature of slag flowing-out (T_f), which was related to capacity of pellet for holding the melt, decreased with the increase of slag former amount and increased with the increase of porosity. This temperature also decreased with increasing of sintering temperature of pellet.

(3) Melting-down temperature of pellet increased with the increase of porosity.

(4) At high temperatures (over 1000 °C), shrinkage was controlled by reduction reaction.

(5) Starting temperature of slag flowing-out (T_f) could be considered as a function of porosity, slag former amount, and sintering temperature. At certain experimental conditions, this temperature for different kinds of pellets could be calculated from Eq. 3.

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