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New Analysis Technique for Sinter Reaction on Simulated Sintering Bed

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Abstract

Improving the properties of sintered iron ore and raising the efficiency of the sintering process are very important for enhancing blast furnace productivity and reducing CO_2 emission. It was difficult, however, to analyze sintering reactions because they are non-uniform reactions of pseudo-grains of a mixture of iron ore and fine coke taking place inside a packed sintering bed. To solve the problem, this study focused attention on local reaction conditions in the bed, and devised a method for simulating sintering reactions under homogeneous environmental conditions. The developed method enables combustion of a specimen of simulated sinter feed under quick heating and downward air flow, the condition peculiar to iron ore sintering, and makes it possible to monitor and analyze in real time the gas arising from the sintering reactions.

1. Introduction

The steel industry uses economical fine iron ore, 5 mm or less in size, after sintering it into lumps called sintered ore. By using strong and highly reducible sintered ore as a main feed material for blast furnaces, it is possible to improve the draft inside the furnace, decrease the consumption of coke, the reducing agent, make the furnace operation stable and efficient, and decrease CO₂ emission.

In a sintering plant, fine ore is mixed with flux limestone and fine coke, which serves as the heat source fuel, and then after water addition, the mixture is formed into pseudo grains. Then at the entry to a sintering machine, the pseudo grains are loaded onto a pallet conveyer composed of iron gratings to form an ore bed roughly 600 mm in depth, ignited at the upper surface of the bed, and while the fine coke burns under downward air flow by suction, the heat generation shifts downwards in the sintering bed, and the pseudo grains are sintered by the heat to turn into ore lumps. This sintering process is suitable for economically producing sintered ore in large quantities, but because of various factors such as the difference in temperature and gas distribution between the upper and lower portions of the ore bed, local unevenness of gas permeability and fluctuation of the composition of the pseudo grains, the structure of sintered ore varies from time to time, which means that the reaction path is non-uniform locally and over time.¹⁾

undersize (5 mm or less) from coke screening, the oversize being charged directly into blast furnaces. To reduce costs, improve productivity and decrease CO_2 emission during the combustion of the fuel, attempts have been made recently to replace fine coke with dry-distilled coal or biomass.^{2, 3)}

The desired properties of the fuel for the sintering process, however, have not been clarified.^{3–5)} On the other hand, it has become clear^{1,4)} that the conventional methods for evaluating the combustion behavior of carbon fuel deal mainly with coal, which burns mainly by decomposition, and are not necessarily suitable for the iron ore sintering process, because of the special combustion condition of ore sintering, namely, the downward air flow through the ore bed by suction and the use of char coke, which burns mainly by surface combustion. For example, pulverization of coal, which is effective with common coal burners, is considered undesirable for ore sintering because it leads to clogging of the ore bed and hinders the air flow, adversely affecting the productivity.¹⁾

The pot test using tens of kilograms of material mixture is widely employed as a method for simulating the real sintering process. However, the real ore sintering process is highly complex and inhomogeneous, and it is difficult to correlate the properties of sintered ore and gases obtained correctly with specific test conditions or process reactions. In addition, it is not easy to conduct the pot test using different materials under different conditions, and therefore, it

The fine coke used as the heat source fuel for the process is the

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is unsuitable for evaluating many types of carbon fuels. While there are several combustion test methods for many types of carbon fuels,⁶ it has not been easy to simulate in laboratories the downward air flow by suction and rapid heating peculiar to the commercial ore sintering process.

In view of the situation and for the purpose of analyzing fundamental sintering reactions, I have developed a method for analyzing the gases arising from the reactions of iron ore sintering whereby it is possible to simulate the downward air suction and rapid heating peculiar to the real sintering process.^{7,8)}

The present paper reports the studies for the development of the test method, the effects of the mixing amount of fine coke in the ore bed over the composition of generated gases, their amounts, and the structure of the product sintered ore, and the change in gas composition depending on the materials involved (ore and alumina).

2. Test

2.1 Test equipment

Figure 1 schematically shows the configuration of the developed equipment for analyzing the gas arising from sintering reactions. The development studies focused on reproducing reactions of the materials under homogeneous conditions while simulating the three characteristic features of the process: (1) the ore bed, (2) the downward air flow through the ore bed by suction, and (3) the rapid heating by ignition.

First, in consideration of (1) and (2) above, a sample holder of silica was designed in the shape of a smoking pipe (see **Fig. 2**). For homogeneous temperature control of the material, the holder had a cylindrical shape roughly 10 mm in diameter and 10 mm in height. The gas from the sample is sucked through the horizontal pipe, and after passing through sensors (an FT-IR, an O_2 sensor, a pressure gauge and a flow meter) arranged in series, it is exhausted by a suction pump. The temperature of the sample is measured using R type thermocouples provided in the holder.

Then, to simulate the rapid heating described in (3) above, an IR lamp made by Thermo Riko Co., Ltd. and a gas heater of a SiC-heating type made by Labotechs were used for sample heating.

When a sample mixture was packed in the holder and heated using the IR lamp so that the gas flow reading of the flowmeter stayed at 0.5 L/min, the sample temperature hit a maximum of 1250°C in 60 s, and the surface layer only of the material was heated and turned into a sintered lump, but there were no fine pores in the sintered layer.

In contrast, when another sample lot was heated with the IR lamp keeping the air flow at 5 L/min in the sample section area, roughly the same air flow rate as in a real sintering machine, the maximum sample temperature was 1 100°C, lower than in the above case, but this maximum temperature was reached in a short time of roughly 40 s. In this case, the sample was sintered also in the surface layer only, but this time the sintered layer had many fine pores. This indicates that an air flow condition similar to that of a real sintering process was maintained. Subsequently, a sample composed only of iron ore was heated using the gas heater under air suction. In this case, the sample temperature hit a maximum as quickly as in 20 to 30 s, but the temperature was below 1 000°C, lower than that by the IR lamp, and the sample was negligibly sintered.

It is clear from the above results that, by single use of any one of the heaters, it was impossible to heat an entire sample lot to make the carbon component burn. After that, tests were conducted using the two heaters in combination. As a result, the material temperature



Fig. 1 Schematic configuration of analyzer for gas arising from sintering reactions (by courtesy of ISIJ⁷)



Fig. 2 Sample holder



Fig. 3 State of coke ignition (light heating temporarily turned off for photographing)

rose to above 1200°C in 20 to 30 s, the carbon component in the mixture burned, and the entire sample was sintered and its color turned black. However, at the beginning of the combined heating tests, only the upper surface of the sample close to the IR lamp was strongly heated selectively, and the temperatures at the upper and lower portions varied from 1200 to 1300°C during the heating.

As a corrective measure, the focus of the IR lamp was shifted downwards to minimize local heating and heat the entire sample evenly. In addition, the gas heater was mounted on rails so that its hot air outlet port could be trained to the desired part of the sample material. By this it became possible to preheat the sample with the port set slightly apart from it and then quickly approach the upper surface to ignite it. It became thus possible to maintain the sample temperature stably at 1 200°C, and sinter an entire sample lot evenly and stably (see **Fig. 3**).

2.2 Simulated sinter materials

Three different sample materials were prepared for the combustion test according to the mixing ratios (a) to (c) given in **Table 1**. Mixing ratio (a) was defined based on the mixing rates of commercial sintering plants. Each of the samples was ground, and after water addition by $100 \ \mu g$, mixed for 5 min in an agate mortar.

	Ore	Alumina	CaCO ₃	Coke
	(mg)	(mg)	(mg)	(mg)
(a)	650.0	0.0	100.0	30.0
(b)	650.0	0.0	100.0	60.0
(c)	0.0	650.0	100.0	30.0

Table 1 Mixing ratios of sinter feed samples

2.3 Test procedures

The test procedure using the developed sintering gas analysis facility is as follows. After mixing the sample materials mentioned in Sub-section 2.2, they were individually packed in the silica holder, the pipe was connected to the gas analyzer, and the air was sucked by the suction pump at a flow rate of 5 L/min. The gas heater, which had been preheated to an exhaust gas temperature of 1000°C, was shifted to the position to heat the sample in the holder, the sample was preheated to 250°C and held at the temperature for 30 s to dehumidify. After all these preparations, the sample was quickly heated by combined use of both the IR lamp at its full capacity and the gas heater.

Through the above procedures, the sample turned red hot, the fine coke in it began to burn, and CO and CO_2 arising from the combustion were detected by the FT-IR. The O_2 content in the exhaust gas decreased after the ignition, but in about 80 s, the combustion gases (CO and CO_2) ceased to be detected, and the O_2 content returned to the level of normal atmosphere.

The test procedure was complete when the combustion gases were no longer detected, whereupon the heaters were switched off.

3. Test Results and Discussion

Figure 4 shows the results of the sintering gas analysis using samples of the three different mixtures described earlier. Here, the point 0 of the abscissa is the time when the quick heating of the sample started after the preheating, and the sample temperature and the change in the exhaust gas composition are plotted along the ordinate.

The samples simulating sinter feed were heated from the preheating temperature 250°C to the maximum of about 1200°C at a rate roughly of 100 K/s, and the change in the concentrations of CO, CO, and O, during the coke combustion was continuously recorded.

To compare the combustion condition by the developed sintering gas analyzer with that in the real sintering process, attention was focused on flame front speed (FFS), which is calculated from the time of gas generation and the sample thickness. The FFS in the test was approximately 20 mm/s, which was substantially equal to the values obtained at large-scale sintering tests and the like. Thus, I considered that the developed analysis method was capable of simulating coke combustion under conditions of the rapid heating and the air flow through the ore bed of the sample sinter feed.

Next, the test results of the combustion of sample materials of different mixtures were compared. With sample (b), the coke content of which was higher than that of the standard sample (a), both the maximum temperature and the CO content were higher than those with (a). With sample (c), which contained alumina in place of iron ore, the CO content was even higher.

From the result of mixture (c) containing inert alumina, the combustion environment of which was likely to lead to incomplete combustion and CO generation, it was inferred that CO that arose from the primary reaction of $C+1/2O_2 \rightarrow CO$ at the surfaces of fine coke



Fig. 4 Comparison of gas concentrations and specimen temperature during sinter reaction

was rapidly blown to the colder lower portion by the downward suction, and as a result, the secondary reaction of $\rm CO+1/2O_2 \rightarrow CO_2$ was decreased.

On the other hand, with mixtures (a) and (b), it seemed that, soon after forming, CO reacted with oxygen in the atmosphere, and

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at the same time, with that in the ore (iron oxide), and turned into CO_{2} .

From the comparison of the result of mixture (b) with that of mixture (a), there seems to be two alternative reasons for the increase of CO in the case of (b): one is that, while CO generation increased as the temperature and the rate of combustion at the fine coke surface rose as indicated by the rise in the specimen temperature, the secondary reaction to form CO₂ was insufficient; and the other is that the reaction $C+CO_2 \rightarrow 2CO$ was accelerated owing to the temperature rise at the fine coke surfaces. More studies are required to estimate and directly measure the coke surface temperature and clarify the reaction route during the sintering process.

Then, the sintered lumps obtained from mixtures (a) and (b) were buried in resin, cut, polished at the sections, and observed through an optical microscope. It became obvious that the structure of sintered ore varied significantly depending on the process condition. As seen in Fig. 5, whereas the sintered lump of mixture (a) consisted mainly of a bright structure of a comparatively high reflectance, that of mixture (b) consisted mostly of a darker structure of a lower reflectance mixed with a fine structure of an intermediate reflectance. From past structural observations, the bright structure is regarded as iron ore that remained unchanged through the process, and the dark and the intermediate types as slag and calcium ferrite that formed through reactions with Ca.¹⁾ With respect to mixture (b), which contained more coke and was sintered at higher temperatures, the following is presumed to have taken place: molten liquid formed in many places in large quantities as the temperature exceeded the melting point of the Fe₂O₂-CaO binary phase diagram, and crystalline calcium ferrite formed during the cooling that followed. In the past, it was not easy by the large-size pot test to estimate the temperature of samples during the process and surmise causal relations



Fig. 5 Optical microscopic observation of sintered samples

of process phenomena, but the specimens obtained through the developed test method can undergo microscopic observation, examination by XRD, etc. Thus, the developed test method proved effective at clearly correlating various process phenomena with the temperature change during the process.

4. Conclusion

A sintering gas analysis method has been developed as a novel technique to clarify the reactions that take place during iron ore sintering, and by this, it has been made possible to analyze sintering reactions under simulated conditions of (1) inside a packed ore bed, (2) downward air flow by suction, and (3) rapid heating, which are peculiar to the industrial iron ore sintering.

Applying the developed method, the gas arising from the combustion of fine coke was analyzed in real time, and the generation amounts of CO and CO_2 were measured during the process. In addition, through microscopic observation of the sintered lumps obtained through the test, it became possible to definitively correlate the product structure with the process temperature.

In the series of tests by the developed method, the composition of the emitted gas and the amounts of its components changed depending on the mixing amounts of fine coke and iron ore (or alumina), which led to a finding that the secondary combustion of CO is markedly changeable during the sintering process. Thus, to select the carbon material most suitable for iron ore sintering and evaluate various alternative fuels, it is necessary to identify the combustion reactions of the carbon material, especially those through which incomplete combustion occurs, and clarify the details of the reactions.

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