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Reduction behavior and crushing strength of carbon-containing iron ore sinters prepared from tar recovered from coke oven gas

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ABSTRACT

The reduction behavior and crushing strength of carbon-containing iron ore sinters (SI–C) prepared from coke oven gas (COG) tar have been examined with a quartz-made fixed bed reactor and with a tensile and compression testing machine, respectively. When an as-received iron ore sinter (SI) is heated at 10 °C/min up to 600 °C in 55% H_2/He, the resulting sample (SI/600) gives a very small, broad pore size distribution profile, the surface area (S_{BET}) and pore volume (V_{BJH}) being 1.5 m^2/g and 0.005 cm^3/g, respectively. On the other hand, SI-pretreated in 55% H_2/He at 450 °C for 4 h (SI-450) provides the pore distribution profile peaking around 10 nm, and S_{BET} and V_{BJH} are 4 m^2/g and 0.02 cm^3/g, respectively. When carbon-containing iron ore sinters (SI/600–C and SI-450–C) are prepared by pyrolysis of the mixture of the pretreated SI and COG tar, no measurable amounts of S_{BET} and V_{BJH} are detectable in any case. The crushing strength of SI-450 is improved significantly by the deposition of tar-derived carbonaceous materials into the pores formed during the pre-treatment. In a temperature-programed heat treatment in He, the evolution of CO, CO_2 and H_2O from the SI-450–C samples start after 600 °C, and each rate profile observed shows a large peak around 700–850 °C. The extent of reduction of SI–C, SI/600–C or SI-450–C is 3, 19 or 55% on SI basis, respectively, and it depends on S_{BET} and/or V_{BJH} of the feed sample.

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1. Introduction

It has been progressing that the development of technology to reduce CO_2 emission by introducing of coke oven gas (COG), which is amplified H_2 by catalyst reforming reaction, instead of the carbonaceous reductant input into a blast furnace in COURSE50 (CO_2 Ultimate Reduction in Steelmaking process by innovative technology for cool Earth 50) project in Japan [1]. As is well known [2–7], the reduction disintegration is due to the reduction of Fe_2O_3 in the iron ore and/or the iron ore sinter (sinter and pellet) to Fe_3O_4 with volumetric expansion, and this causes a loss in a permeability in the blast furnace. This reduction disintegration also may occur in a blast furnace using reforming COG, because the reduction rate is larger than the conventional method using coke [7]. In addition, it is believed that the increase in the reduction rate can decrease the thermal reserve zone temperature, and it leads a low reducing agent rate in the operation of the blast furnace. Therefore, the development of technology for the production of carbon-containing sinter ore composite having high-reactivity and low-reduction disintegration index may be very important.

The production methods for iron ore-carbon composites from iron ore and carbonaceous materials, and the examination of composite reduction behavior have been reported by several researchers [8–25]. The iron ore–carbon composite prepared by the chemical vapor infiltration (CVI) method, in which tar-containing gas is generated by the pyrolysis of carbonaceous resources that are deposited into nano-scale pores (produced by the dehydration of limonite), is possible to achieve rapid reduction compared to the conventional reduction method using metallurgical coke. This is because the contact area between iron oxide and carbon deposited by CVI is higher [8–14]. However, the CVI method has a problem in that the amount of carbon deposition is small, 3–5 mass%-dry per experimental run. Although this problem is due to the scale of the experimental unit and/or conditions, the strength of the resulting composite has been not examined [8–14]. On the other hand, iron oxide-carbon composites prepared from a mixture of thermal plastically carbonaceous materials (resin or coal extract) and limonite has been investigated. In this method, carbon is loaded into nanometer-sized pores formed by the simultaneous de-hydration of limonite and softening of carbonaceous materials during heat treatment of the mixture [15,16]. Although this procedure can achieve a high amount of carbon loading and high reactivity, the particle size of limonite used is limited to the nano- and micro-scale. Grinding of larger particles to the nano-scale requires a considerable amount of energy, and in addition, the examination of the strength of the composite has not been performed. Besides the two methods described above, the tar impregnation method has also been reported [24,25]. The composite is prepared from tar-liquid recovered from the pyrolysis of carbonaceous resources and is impregnated into nanopores previously produced by limonite dehydration. Compared to the CVI treatment, it is possible to not only introduce a larger amount of carbon into the pores, but also achieve

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improved strength [25]. Therefore, the carbon-containing iron ore composite is expected to undergo rapid reduction as well as low-reduction disintegration during reduction. However, the above reports only target limonite having a large combined water amount to produce porous-ore, and the possibility of application for iron-ore sinter (SI) has been not investigated, because sintered ore does not have suitable mesopore for deposition of carbonaceous materials.

In this study, therefore, we firstly investigated the most suitable conditions for production of porous-SI in detail, and carbon-containing iron ore sinters (SI–C) were prepared from COG tar and SI or porous SI. The reduction behavior and crushing strength of SI–C were then examined with a quartz-made fixed bed reactor and with a tensile and compression testing machine, respectively.

2. Experimental

2.1. Sample

Agglomerated iron ore sinter (SI) was supplied by the Japanese steel company and used in this work. It was first ground and then sieved into SI particles with a size fraction from 2.0 to 3.4 mm. The composition on a dry basis is as follows; total-Fe, 57; FeO, 8.2; CaO, 9.4; SiO_2, 6.2; Al_2O_3, 1.7; MgO, 1.4 mass%; and basicity, 1.54. The specific surface area (S_{BET}) and pore volume (V_{BJH}) were <1 m^2/g and <0.001 cm^3/g, respectively. COG tar recovered from the actual coke production process was supplied by the Japanese chemical company and used in this study as the carbon source. The elemental analysis results are as follows; C, 91; H, 5.3; N, 1.1; and S, 0.5 mass%-dry.

2.2. Pretreatment of SI

The preparation of SI samples with different pore structures was carried out with a flow-type fixed bed quartz-made reactor. About 1.0 g of SI was first charged into an alumina cell, which was then placed at the center of the reactor. After the air in the reactor was replaced with high-purity He (>99.9999%), the He was switched to 55% H_2/He at 200 cm^3 (STP)/min. In the non-isothermal reduction run, the reactor was finally heated at 10 °C/min to a predetermined temperature (400–1000 °C) in a stream of 55% H_2/He and quenched to room temperature in He. In the isothermal reduction run, the sample was first heated up to 400–600 °C under He in the same manner as above, and then exposed to a stream of 55% H_2/He to reduce the SI. The reduction was carried out in 0–720 min. The flow rate of high-purity He or 55% H_2/He was 200 cm^3 (STP)/min in both cases. The temperature was determined using a K-type thermocouple inserted at the bottom of the cell. The amount of H_2O that evolved during the reduction was on-line measured at intervals of 2 min with a photo-acoustic multi-gas monitor (Innova). In this study, for example, SI/600 means reduction up to 600 °C at 10 °C/min (non-isothermal reduction), and SI-450 shows the reduction at 450 °C for 4 h (isothermal reduction).

2.3. Preparation of carbon-containing SI

The as-received SI and pretreated-SI prepared in Section 2.2 were used for the preparation of the composites. These samples were first charged into an alumina cell, and COG tar was then added into the cell at room temperature. The weight ratio of tar against SI samples was equal to 2.0. After physical mixing of the SI samples and tar, the cell was heated at 10 °C/min to 500 °C in a stream of high-purity He at 200 cm^3 (STP)/min to produce composites using the above-mentioned reactor.

2.4. Reduction experiment and gas analysis

The reduction behavior of SI-samples (SI, pretreated-SI and the composites prepared from COG tar and SI or pretreated-SI) were investigated in the same manner as described in Section 2.2. After SI, pretreated-SI or the composite was charged into the cell and placed at the center of the reactor. Then, high-purity He was introduced at 200 cm^3 (STP)/min into the system, and the effluent was analyzed using a high-speed micro gas chromatograph (GC) (Inficon) to ensure that the remaining air was replaced with the He until the N_2 concentration in the reactor outlet gas decreased below 30 ppm. The reactor was finally heated at 10 °C/min to a pre-determined temperature (500–1000 °C) in a stream of He or 55% H_2/He and then immediately quenched in He flow to room temperature. The amounts of CO, CO_2, CH_4 and H_2O evolved were on-line analyzed by GC and gas-monitor at intervals of 3 and 2 min, respectively. The extent of reduction was estimated by the following equation:

$$\text{Extent of reduction } (\%) = \frac{\text{Total amount of } O\text{—containing gas evolved } (mol\text{—}O/g)}{\text{Amount } O \text{ in samples } (mol\text{—}O/g)}. \quad (1)$$

2.5. Characterization

The iron forms in the as-received SI, pretreated-SI, composites and the samples after reduction experiments in He or 55% H_2/He were measured with a powder X-ray diffractometer (XRD) (Shimadzu) using Mn-filtered Fe-Kα radiation, which was used at a generator setting of 40 kV and 30 mA. The samples were first loaded in a glass holder for measurements after crushing, and the XRD patterns were then collected over the range 20–70° at a speed of 2°/min (2θ) and a scan step of 0.01°. The pore structure of the samples was analyzed using a nitrogen adsorption measurement equipment (Quantachrome Instruments). The samples were first dried at 108 °C under vacuum for 1 h in a glass cell, and then high-purity N_2 (>99.9999%) gas was adsorbed/desorbed at the liquid nitrogen temperature of −196 °C. The S_{BET} and V_{BJH} values were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Hallender (BJH) methods for the obtained N_2 isothermal curves, respectively.

The crushing strength of SI, pretreated-SI, the composites or the samples after reduction experiments in He or 55% H_2/He was determined using a tensile and compression testing machine (Minebea) according to the Japanese Industrial Standards (JIS M 8718). The test conditions in the compression mode were speed of 5 mm/min and a maximum load value of 500 N. The test was performed 10–20 times per sample, and the average value was employed.

3. Results and discussion

3.1. Changes in pore structure and iron forms in SI during heating reduction

Fig. 1 shows the formation rate, cumulative amount of H_2O (Fig. 1a), and the reduction behavior (Fig. 1b) estimated by the amount of H_2O evolved during non-isothermal reduction in 55% H_2/He. The cumulative amount of H_2O was calculated by an integration of the formation rate curve. The evolution of H_2O (Fig. 1a) started from 400 °C, and SI showed a broad profile with two unresolved peaks at around 650 and 750 °C, respectively. The cumulative amount of H_2O increased linearly from 600 to 800 °C and reached to approximately 12 mmol/g at 1000 °C. The reduction of SI (Fig. 1b) started from 400 °C, and >90% reduction rate was observed above 900 °C.

Fig. 2 presents the changes in the pore size distribution of pretreated-SI up to 500 or 600 °C, as an example, and the S_{BET} and V_{BJH} values during non-isothermal reduction of SI. Pore sizes of <100 nm were nearly not seen in SI and pretreated-SI at 500 °C (Fig. 2a), whereas pores of 2–60 nm having a weak peak around 10 nm were observed in pretreated-SI up to 600 °C (Fig. 2b). This pore size distribution at 600 °C tended to be retained even at increasing

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