Analysis of Reducing Characteristics of Direct Reduced Iron using Blast Furnace Dust

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ABSTRACT

Industrial by-products generated by integrated iron and steel manufacture cause environmental pollution. The by-products contain not only iron element but also harmful substances. Therefore, in view of to waste recycling and environmental preservation, production of sponge iron using the by-product is considered an effective recycling method. In this study, reduction efficiency of pellets from blast furnace dust was measured. Metallization was found to be increased, as C/Fe_{total} ratio and reaction time were increased. The pellets were formed into a globular shape, and calcined for 60 minutes at 1100°C in an electric furnace. Phase changes were analyzed using an X-ray diffractometer. Microstructures of the pellets were observed by a scanning electron microscope.

Key words : Blast furnace dust, Metallization, Waste recycling, Sponge iron

1. Introduction

Recently, the demand stagnation of China accounting for about 50% of the global steel demand is affecting slow-down in the steel demand. As a result, the prices of iron ore and iron scrap have been dropped since 2013 due to supply surplus phenomenon of raw materials for steel. Therefore, use expansion of low-cost raw materials and production technologies for high-quality iron sources are being required for reinforcement of steel companies' competitiveness resulting from lowered price competitiveness of direct reduced iron. As the dust, sludge, etc. currently produced in steel-making processes contain iron oxides, there are advantages in their use as a substitute raw material for iron ore to produce direct reduced iron.^{1,2)} Among the advantages, blast furnace dust as a representative byproduct of steelmaking process has a very high content of iron oxide so as to facilitate manufacturing of direct reduced iron.

Global production of direct reduced iron in 2014 was 75 million tons, or a scale grown by about 95 times as compared with 1970 (790,000 tons), of which 33 million tons were produced in Asia/Oceania, 19 million tons in Mideast/North Africa, and 13 million tons in Latin America including Mexico, etc. The domestic market of reduced iron is dependent on import volumes, and about 500,000 ~ 600,000 tons were annually imported from India, Venezuela, etc.³⁾ However, as the drop in prices of iron ores is extended over a long period, domestic steel manufacturers are almost not

importing any direct reduced iron.

In general, direct reduced iron is reduced and manufactured from iron ores in solid state, where coal or carbon monoxide is used as a reducing agent (see Fig.1). Stepwise reduction reaction of iron oxide proceeds in the order of Fe₂O₃ (hematite, HCP) → Fe₃O₄ (magnetite, cubic) → FeO (wustite, cubic) → Fe (metallic iron, BCC or FCC), and may be represented as shown by the following expressions 1, 2 and 3.^{4,5)}

In the present study, manufacturing experiments of direct reduced iron were conducted by using blast furnace dust produced as a byproduct from steelmaking process. In the present experiment, green compacts of blast furnace dust and anthracite were mixed together and sintered for reduction characteristics analysis of the direct reduced iron, where reduction efficiency and phase transition characteris-

Fig. 1. Cross-section of a partially reduced porous iron ore pellet.

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Table 1. Chemical Analysis of Blast Furnace Dust

(unit:wt%)

No.	Total Fe	Metal Fe	Al ₂ O ₃	CaO	SiO ₂	C	S
Blast furnace dust	61.5	1.3	0.7	1.4	2.6	5.8	0.3

Table 2. Chemical Analysis of Coal

(unit:wt%)

Anthracite	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	S	LOI
	1.8	0.6	0.3	1.1	0.3	0.4	95.5

tics were analyzed and evaluated.

2. Experimental Procedure

2.1. Starting raw material

In the present study, blast furnace dust as a steelmaking byproduct was used for manufacturing of direct reduced iron. For coal, domestically produced anthracite was used, with the chemical compositions of blast furnace dust and anthracite as a reducing agent being shown in Table 1 and 2. Table 3 shows the proximate analysis of Anthracite coal, fixed carbon found to be 84.6%, moisture 1.6%, ash 5.8%, volatile matter 7.9%. The blast furnace dust is an iron-containing byproduct with total Fe content of 61.5 wt%, and a mean particle diameter of 35 μ m. Ignition loss of the domestically produced anthracite was 95.5 wt%, and the fixed carbon content 84.6 wt%. In addition, an XRD pattern for blast furnace dust as the raw material is shown in Fig. 2, most of which is present in the form of Fe₂O₃.

2.2. Preparation and analysis of specimens

Blast furnace dust is in a fine powder form of 35 μ m in mean particle diameter, and feeding becomes difficult due to scattering by the in-furnace heat flow and the produced gas when fed in a powder state. Therefore, it should be fed by controlling its size and shape so as to have a given specific weight. Thus, in the present study, manufacturing of

globular green compacts was attempted by mixing blast furnace dust with water. Here, the ratio for fine dust and water was fixed at 30%, and the weight of green compact at 3 g. Diameters of thus-produced green compact pellets were around 10 mm. They were dried under 120°C condition until a constant weight was obtained. The green compacts subjected to constant-weight drying were mixed with anthracite as the reducing agent and then loaded into an alumina crucible, where the mixing ratios between green compact and anthracite were controlled to be 1 : 0.5, 1, 1.5, and 2. Subsequently, the alumina crucible was positioned in an electric furnace and held at 1100°C for 0 min, 20 min, 40 min, and 60 min. Reduced iron out of the furnace was then subjected to the analysis for crystalline phases using an X-ray diffractometer (Dmax2500, Rigaku, Japan). Shapes of the reduced iron were observed using a stereoscopic microscope, and microstructures were examined using a scanning electron microscope (SM-300, Topcon). In addition, Total Fe and metallic Fe were found by wet and instrumental analyses, and reduction efficiencies were calculated according to the expression (4).

$$\frac{\text{Metal Fe (wt\%)}}{\text{Total Fe (wt\%)}} \times 100 \quad (4)$$

3. Results and Discussion

3.1. Reduced iron shape

Reduced iron of blast furnace dust in globular shape produced in different mixing ratios and reduced for different times was observed using a stereoscopic microscope, as shown in Fig. 3. As indicated in Fig. 3, multitude of radial cracks were produced across the cross section for the mixing ratio of the green compact and anthracite 1 : 0.5 and reduction time of 60 min. Radial cracks increased with smaller proportion of anthracite and longer reduction time. In general, direct reduced iron is manufactured by reaction between iron oxides inside iron ore and solid carbon or reducing gas (carbon monoxide, etc.).⁶⁾ Oxygen content is increased as the iron oxide content present in iron-containing products is increased, and this oxygen escapes as carbon dioxide in the reduction process.^{7,8)} At this time, oxygen sites within iron oxide remain as a vacant space, which was considered to act as a source for crack generation during calcination shrinkage.⁹⁾

As shown in Fig. 1, reduction of iron oxide generally occurs from the surface, and then gradually extends inward.

Table 3. Analysis of Coal

Anthracite	FC, ad/%	M, ad/%	A, ad/%	V, daf/%
	84.6	1.6	5.8	7.9

Fig. 2. XRD pattern of blast furnace dust.

Fig. 3. Morphology of DRI of different mixing ratios and reduction times.

Here, the center part of reduced sintered body is known to consist of hematite crystals, sequentially followed by formation of magnetite, wustite and porous metal iron on the surface layer.⁸⁾ The extension of the reduction front the surface into the center of the pellets with increasing reduction time can be seen in the images of Fig. 3. Gray rims indicating the inward moving of reduction boundary can be distinguished for the reduction time 20 min. In general, upon reduction reaction between iron ore and anthracite, the reducing gas (CO) is diffused into the sphere interior, and the produced gas (CO_2) is moved to outside of the sintered body.^{10,11)} Consequently, vacant spaces of oxygen atoms resulting from oxygen breakaway are increased with increase in sintering time, which facilitates movement of reducing gas, etc. In the present experiments, diffusion of grey part up to sphere interior was also affirmed in the sintered body with 60 min of reduction under the mixing condition of 1 : 2 between blast furnace dust and anthracite. Based on this observation, reduction reaction is presumed to have occurred throughout the sphere cross section.

3.2. Microstructure of reduced iron

To observe microstructures in different mixing ratios between green compact of blast furnace dust and anthracite, a scanning electron microscope was employed, the results of which are shown in Fig. 4. In all prepared specimens, the particle sizes of sintered body with 10 min of reduction were not constant, and presence of a small amount of pores could also be observed. At the reduction time of 60 min, particle size and distribution were homoge-

nized, and ellipsoidal particles appear to have surface dissolved. With increasing reduction time from 10 to 60 min, particle or grain growth, decrease in fine pores and densification have occurred. This is also the result similar to that of iron oxide reduction published by Wagner *et al.*¹²⁾ Wagner *et al.* have made an observation of microstructures as a function of reduction time, where ellipsoidal and linear particles and fine pores were also present in the reduced iron.

The reduction condition of 10 min for all green compacts was considered to involve a reduction stage where phase transformation occurred from hematite (Fe_2O_3) to magnetite (Fe_3O_4), which could be inferred from the volume increase (20%) of a sintered body.¹³⁾ Most particles had a size of around 10 μm , and nonuniform particles were also observed. At the reduction times of 20 min and 40 min, wustite (FeO) particles in ellipsoidal shape were presumably produced and the neighboring particles appeared to have agglomerated together, which cause the deformation of the pellets from inside. For the reduction time of 60 min, the crystal structure was transformed from wustite (FeO) to iron (Fe), where Fe crystals were grown by being connected to the surrounding particles on the particle surface.¹⁴⁾ Therefore, Fe particles were considerably continuous with presence of pores.

Particle size under the reduction time condition of 60 min was 10 ~ 20 μm , with pore size also being on the level less than 20 μm , which is the form similar to the reported microstructures of the existing reduced iron.¹⁵⁾ The reduced particles were grown into ellipsoidal and linear forms with increase in CO and reduction time, and wustite (FeO) was

Fig. 4 Microstructure of blast furnace dust DRI.

observed as a part with the particle surface being small and bright. Particle growth from wustite (FeO) to iron (Fe) requires a reduction time, and the initial oxygen content is known to have a large effect.¹⁶⁾ Therefore, oxygen break-away is being reported to be increased as the initial iron oxide content is increased, and to have a favorable effect on iron particle growth.¹⁷⁾

3.3. Crystallinity analysis of reduced iron

For crystallinity analysis of reduced iron from blast furnace dust, an X-ray diffractometer was employed, and respective XRD patterns for different mixing ratios between green compact and anthracite are shown in Fig. 5. Major crystalline phase of blast furnace dust prepared in pellets before calcination was Fe_2O_3 , and Fe peak intensity was increased in (a) and (b) under the reduction time condition of 20 min, while FeO peak intensity was increased in (c) and (d). In addition, iron oxide could also be seen to remain in the sintered body. Under the reduction condition of 40 min, Fe peak intensity was increased in all of (a), (b), (c), and (d). Particularly, Fe crystals were primarily observed under the condition of 60 min so that most of iron oxides could be confirmed to have been reduced. Changes in crystal phases occurred in the order of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ with

increase in the reduction time and the mixed amount of anthracite. The increase in reducing agent anthracite was considered to have an effect on Fe crystallinity as indicated by the increase in Fe peak intensity.

3.4. Reduction efficiency of reduced iron

Total Fe and metallic Fe of all sintered bodies in different mixing ratios between blast furnace dust pellets and anthracite and reduction time changed were subjected to wet and instrumental analyses (KS E ISO 2597-1, 5416), and the corresponding calculated reduction efficiencies are shown in Table 4. Initial total Fe content of blast furnace dust was 61.5 wt%, and the reduction efficiencies together with total Fe and metallic Fe contents showed a gradual increase with increase in reduction time. For the reduction time 60 min, the respective reduction efficiencies of the mixing ratios 0.5, 1, 1.5 and 2 were 69.4 wt%, 74.2 wt%, 88.9 wt%, and 96.8 wt%. The increase in the reduction time and the mixed amount of anthracite at a given reduction temperature was considered to have an enormous effect on improvement of reduction efficiency.

Figure 6 shows a graph of reduction efficiencies as a function of mixing ratios between blast furnace dust and anthracite as well as reduction time, displaying the increase in

Fig. 5. XRD patterns of DRI.

Table 4. Chemical Analysis of Blast Furnace Dust

Reduced time(min)	Dust/coal Ratio	Chemical Analysis (wt%)		Metallization degree (%)
		Total Fe	Metal Fe	
10	0.5	67.8	1.0	1.5
	1	68.2	1.0	1.5
	1.5	69.2	1.3	1.9
	2	71.2	5.3	7.4
20	0.5	74.1	14.8	20.0
	1	74.1	20.1	27.1
	1.5	77.6	22.0	28.4
	2	77.9	23.2	29.8
40	0.5	78.2	30.6	39.1
	1	79.5	33.7	42.4
	1.5	80.2	35.4	44.1
	2	80.4	38.1	47.4
60	0.5	80.5	55.9	69.4
	1	80.9	60.0	74.2
	1.5	81.2	72.2	88.9
	2	84.1	81.4	96.8

reduction efficiency with increase in reduction time. Although almost no reduction occurred in all sintered bodies under the reduction time condition of 10 min, the reduction efficiency was drastically increased at the reduction time of 40 min. Subsequently, large differences in reduction efficiencies between mixing ratios were observed for the reduction time of 60 min. Here, the reduction efficiency of

Fig. 6 Metallization degree vs reduction time.

the sample in mixing ratio 1 : 2 between green compact and anthracite was 96.8 wt%, and for the mixing ratio 1:0.5 69.4 wt% which is decreased by 27.4 wt%. The results showed that the reduction reaction rate was slowed down when the mixed amount of anthracite was insufficient compared with blast furnace dust and the reaction rate was high when the amount was sufficient. In addition, the reduction efficiency of iron oxides published by Liu and Strezvov exceeded 90 wt%,¹⁸⁾ which was a comparable level to the reduction efficiency of blast furnace dust in the present work.

4. Conclusions

In the present study, changes in crystal phases and reduction efficiencies of direct reduced iron were observed for dif-

ferent mixing ratios mixing ratio between blast furnace dust and anthracite, and the following conclusions have been drawn.

1) The increase in radial cracks with increase in reduction time was observed. In addition, it was also observed that the grey rim developed from the surface extends inward. The phenomena presumably indicate the reduction process inside the pellets. For the reduction time of 60 min, even the center of the cross section of the pellets changed to grey color.

2) With increase in reduction time, particle size and distribution became homogeneous, fine pores increased, and particle densification occurred. The particle size at the reduction time of 60 min was about 10 ~ 20 μm , and around 10 μm at the reduction time of 10 min, and particles grew into ellipsoidal and linear shapes with an increase in reduction time.

3) Phase transitions in the blast furnace dust proceeded in the order of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Fe and FeO phases were increased for the reduction time 20 min. At the reduction time of 60 min, iron oxide crystals were greatly reduced, and metallic Fe phase was primarily observed. In addition, Fe crystallinity became higher with increase in reduction time and mixed amount of anthracite.

4) Reduction efficiency exhibited a close correlation with mixing ratios between blast furnace dust and anthracite as well as reduction time. The highest reduction efficiency (96.8 wt%) was observed when the mixing ratio between blast furnace dust and anthracite was 1 : 2 and the reduction time was 60 min.

5) Blast furnace dust exhibited reduction characteristics similar to those of the existing high-grade iron ores as reduction time and mixed amount of anthracite were increased. Consequently, blast furnace dust was suggested to be used as a substitute material for the iron ores in manufacturing of direct reduced iron.

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