Direct Reduction Behaviors of Composite Binder Magnetite Pellets in Coal-based Grate-rotary Kiln Process

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(Received on June 10, 2010; accepted on October 25, 2010)

Directly reduced iron is an imperative burden for EAF (electric arc furnace) to make good quality and special steel. As an alternative of direct reduction processes, an innovative coal-based direct reduction of composite binder magnetite pellets in grate-rotary kiln has been developed at Central South University and put into operation. A study of the direct reduction behaviors of composite binder magnetite pellets was carried out in a simulating coal-based grate-rotary kiln process in this paper. Preheated pellets made of magnetite concentrate and composite binder and fired oxide pellets containing bentonite as binder were directly reduced using non-coking coal as reductant in a tube furnace, and their reduction behaviors have been demonstrated by measuring reducibility, variations of compress strength, porosity, phases changes and microstructure under XRD, SEM and optical microscopy. It is shown that preheated pellets possess much better reducibility than fired oxide pellets. Superior reducibility of preheated pellets should be ascribed to their higher effective diffusivity due to higher porosity. The compressive strength of preheated pellets climbs quickly after reducing for 30 min and achieve a high value at the end of reduction, leading to smooth and intact metallized pellets whereas the compressive strength of metalized pellets from reducing of fired pellets is much lower, more cracks and fractures being formed. The preheated pellets possess self-curing function because of the multiple functions of composite binder, eliminate cracks and fractures and keep pellets intact during reducing, depressing reduction degradation and preventing accretion in rotary kiln.

KEY WORDS: magnetite concentrate; direct reduction; preheated pellets; fired oxide pellets; coal-based grate-rotary kiln.

1. Introduction

Directly reduced iron (DRI, or called sponge iron) has been found an excellent feed in electric arc furnace (EAF) steelmaking, which has low tramp element content and steady component as a substitute for scrap, it is generally preferred in the production of high quality steel.1–3) Nearly 59.8 million tons of DRI were produced in 2006 over the world, some 80% of which were produced by gas-based processes, the left by coal-based processes. However, total DRI output continued to increase and reached 68.8 million tones even confronted with economical crisis in 2008; coal-based DRI was increased up to 17.6 million tons amounting for 25.7% of total DRI production due to higher natural gas price. However, the DRI capacity is only 750 thousand tons in China in 2008. In the meantime, the EAF production has exceeded 40 million tons annually, and most of EAF operate on hot metal as feed.4)

In order to push forward the development of DRI production, many DRI processes have been investigated5–7) including gas-based process and coal-based direct reduction of composite binder pellets. Due to lack of high grade lump iron ores and natural gas more attentions have been paid to coal-based direct reduction of pellets processes in China. However, there are some disadvantages for the traditional coal-based rotary kiln process using fired oxide pellets as burden, the so-called two-step processes, especially the reduction degradation of fired pellets during reduction because of phase transferring from hematite to magnetite, leading to reduction swelling and kiln accretion. One DRI plant utilizing the latter process with an annual output of 150 thousand DRI has been put into operation since 2007, where grate-rotary kiln process was utilized and the kiln accretion was eliminated in the process of coal-based direct reduction of composite binder pellets.8)

Based on the previous researches of reduction kinetics and process parameters optimization of coal-based direct reduction of composite binder pellets,9) so called one-step process, reduction behaviors of coal-based direct reduction of composite binder magnetite pellets using non-coke coal as reductant were investigated to elucidate the mechanism of how to eliminate kiln accretion, which is usually unavoidably confronted in the two-step DRI processes.

2. Experimental

2.1. Raw Materials

Experimental materials include magnetite concentrate,
bentonite, and noncoking coal, which are all sourced locally from Xinjiang. And composite binder FH (major components of sodium humate) is produced according to the invention patent held by Central South University. Chemical analysis of the magnetite concentrate, bentonite and coal used in the experiments are shown in Tables 1, 2 and 3, respectively.

The fineness of magnetite concentrate is 55.5% and 80.1% passing 0.044 mm and 0.074 mm, respectively. The morphology of magnetite particles under SEM was depicted in Fig. 1.

The coal samples produced from Xinjiang is of bituminous type. Its chemical analysis, industrial analysis and ash softening and melting properties were measured and tabulated in Tables 4 and 5, respectively. It can be seen that the Xinjiang coal is suitable for direct reduction.

### 2.2. Experimental Procedure

The experiment flowsheet to simulate the innovative one-step process include proportioning pellet feeds, mixing, balling, drying, pre-heating of green balls in oxidizing atmosphere and reducing hot preheated pellets by using coal as reductant, referred to the literature. Green balls were made of 1.5% composite binder FH and Xinjiang magnetite concentrate in a disc pelletizer (diameter 1000 mm, rim height 300 mm, angle of inclination 45° and rotating 28 rpm). The finished green pellets were dried in the oven at 105°C for 4 h for further experiment. Preheating and reduction of pellets were carried out in stainless steel pot (diameter 65 mm, depth 100 mm) using an electrically heated tube furnace of 800 mm long and inside diameter of 80 mm. After stainless steel pot was heated at 900°C for 15 min, dry pellets were put in. When preheating of pellets was finished, reduction coals (mass ratio of coal to pellets is 2 in order to keep enough reducing atmosphere) were loaded into the stainless steel pot. And the pot was moved to the highest temperature area of shaft tube furnace for reduction of hot preheated pellets to take place.

The tests flowsheet to simulate the two-step process, i.e. the reduction of the fired oxide pellets is a little different from the above. Green balls were made of 1.5% bentonite and magnetite concentrate, and then dried for further preheating and firing in tube furnace to prepare fired oxide pellets for the following reduction tests. Green balls were hardened by preheating at 800°C for 10 min, firing at 1150°C for 20 min and cooling to produce fired oxide pellets. The cooled oxide pellets would be loaded into the shaft tube furnace for reduction of hot preheated pellets to take place.

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ent density ($\rho_1$) and true density ($\rho_2$). Chemical analyses and other test data were obtained by corresponding ISO standards. The reducibility of pellets was evaluated by their reduction index and metallization degree based on mass loss measurement and chemical analysis, respectively. Microstructure of pellets was measured by using SEM and optical microscopy. And phases transferring during reduction were determined by X-ray diffraction.

3. Results
3.1. Reducibility of Pellets

Reduction index against reduction time is depicted in Fig. 2. Reduction index increases dramatically with an extension of reduction time. Then the reduction index reaches steady when reducing for about 60 min and 100 min for preheated pellets and fired oxide pellets, respectively. It can be concluded that preheated pellets possess better reducibility than fired oxide pellets.

Figure 3 shows the dependence of metallization degree on reduction time. It is very interesting that metallization degree of both types of pellets is very similar to each other before reducing for 15 min. However, metallization degree of preheated pellets increases dramatically while metallization degree of oxide pellets increase slowly after reducing for 20 min. The metallization degree of preheated and oxide pellets amounts to 82.1% and 61.3%, respectively when reducing for 40 min. Especially the time for preheated pellets to reach the metallization degree of over 90% is only 50 min whereas over 80 min for oxide pellets. This agrees with that of Fig. 2, preheated pellets possess better reducibility.

Above results are proven by that in Fig. 4, where lots of FeO appear earlier during the reduction of preheated pellets than fired oxide pellets. Also the content of FeO declines much quickly during reduction of preheated pellets.

3.2. Phases Transferring During Reduction

X-Rays diffraction of preheated and oxide pellets were summarized in Fig. 5 and Fig. 6. It is shown that main phases are hematite and magnetite inside of preheated pellets and fired oxide pellets, respectively. It can be concluded that preheated pellets possess better reducibility than fired oxide pellets.

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lot of metal iron and wustite dominate in preheated pellets when reducing for 40 min.

In contrast, hematite dominates and only minor magnetite exists in oxide pellets before reduction. However, hematite disappears only after reducing for 15 min. Moreover, magnetite still exists when reducing for 40 min. It can be inferred that the reduction kinetics conditions of preheated pellets are superior to that of oxide pellets, leading to preheated pellets being reduced much more quickly than oxide pellets.

3.3. Structure Variations of Pellets

3.3.1. Compressive Strength of Pellets during Reduction

Figure 7 reveals the variations of the compressive strength of pellets with reduction duration. The compressive strength of both preheated pellets and fired oxide pellets decreases dramatically and drop to valley when reducing for 20 min. Compressive strength of preheated pellet drops from 540 N/pellet to 50 N/pellet and the minus gain is 90.3% while fired oxide pellet decreases from 3340 to 210 N/pellet and the minus gain is 93.6%. However, the compressive strength of preheated pellet soars compared to a slow increase for oxide pellets after reducing for 40 min. The final compressive strength of metallized pellets from preheated pellets and oxide pellets after reducing for 100 min is 2590 N/pellet and 850 N/pellet, respectively, which agrees with Fig. 2 and Fig. 4 due to superior reducibility of preheated pellets. It also can be found that there is a close relationship between metallization degree and compressive strength of pellets during reducing. In the meantime there are other factors affecting the compressive strength of reduced pellets because there is a huge difference in compressive strength of the two types of reduced pellets.

3.3.2. Macrostructure of Pellets during Reduction

The dramatic decrease in the compressive strength of reduced pellets is partly ascribed to some breakage and cracks of pellets forming during reduction. As shown in Fig. 8, there is little difference in the unbroken pellets proportion before reducing for 20 min, then the unbroken pellet percentage of preheated and fired oxide pellets decreases with an extension of reduction time and drops to the valley for about 30 min.

However, the unbroken proportion of preheated pellets reaches 100%, which means cracks of preheated pellets disappeared at the end of reduction. However, about 10% reduced pellets from oxide pellets are broken or possess cracks, as shown in Fig. 9.

More cracks and broken pellets mean that higher degradation occurs due to the reduction of hematite into magnetite, leading to much higher risk in kiln accretion. This probably can explain why the kiln accretion can not be eliminated in the traditional two step direct reduction.

![Fig. 6. XRD pattern of oxide pellets during reduction (mass ratio of coal to pellet=2, reduction at 1050°C).](image)

![Fig. 7. Compressive strength vs. reduction time (mass ratio of coal to pellet=2, reduction at 1050°C).](image)

![Fig. 8. Comparison of unbroken pellet percentage between preheated pellets and fired oxide pellets (mass ratio of coal to pellet=2, reduction at 1050°C).](image)

![Fig. 9. Photos of reduced pellets after reduction for 100 min, (a) reduced product of preheated pellets; (b) reduced product of oxide pellets.](image)
process, where oxide pellets are used as burden.

Pellets macrostructure for different reduction time were shown in Fig. 10, where the development of cracks and fractures can be found. It can be seen that concentric cracks dominate while minor radial cracks occur inside reduced pellets during the reduction of preheated pellets, and these cracks only exist in interior layers of pellets. With the reduction continuing, metal iron grains grow up, reduced pellets shrink and the cracks disappear, smooth and intact reduced pellets being produced as shown in Fig. 9(a). Therefore, preheated pellets possess “self curing function” to eliminate cracks and fractures during reducing. However, oxide pellet produces some long radial cracks, which exist through the whole pellet and reach the surfaces, destroying the pellet structure. And some of oxide pellets turn into many fragments due to stress during reduction as shown in Fig. 9(b). Usually the process is irreversible.

From the photographs (Fig. 10), reduction of fired oxide pellets is primarily confined to shrinking un-reacted-core model. However, reduction of preheated pellets seems to agree with volumetric model due to their micro structure and the functions of composite binder.

4. Mechanism of Superior Reducibility and Eliminating Degradation

4.1. Porosity Changes

According to pycnometer method, porosity of reduced pellets was measured. The porosity change was given in Fig. 11. At the beginning of reduction, porosity of preheated pellets and oxide pellets are 19.9% and 14.8%, respectively. With an increase in reduction time from 5 to 30 min, porosity of preheated pellets and oxide pellets both increases rapidly. Over 30 min, porosity of oxide pellets increases slowly, but porosity of preheated pellets still increases dramatically, when reduction duration reaches 60 min, porosity of preheated pellets reaches the peak, then drop slightly. Obviously, porosity of preheated pellets is higher than oxide pellets’ during the reduction.

Usually, at the early reduction of iron ores, the overall rate is controlled by the rate of chemical reactions. And in the middle of reduction, the overall rate is controlled by the diffusion. Different porosity always means different diffusivities. At the end of reduction, the product of coal gasification is mainly monoxide carbon. Using Chapman–Enskog equation:

\[ D_{AB} = 1.8829 \times 10^{-22} \left( \frac{T^3(M_d^{-1} + M_B^{-1})^{1/2}}{p\sigma_{AB}^2\Omega_{AB}} \right) \] (1)

Where \( p \) is the pressure (Pa), \( D_{AB} \) is in m\(^2\)/s, \( T \) is the temperature (K), \( M \) is the molecular mass (kg), \( \sigma_{AB} \) is a constant in the Lennard–Jones potential function, and \( \Omega_{AB} \) is the collision integral. Under the conditions of 1050°C and

![Fig. 10. Macrostructure inside pellets during reducing.](image)

![Fig. 11. Pellet Porosity change during reduction of preheated pellets and fired oxide pellets (mass ratio of coal to pellet=2, reduction at 1050°C).](image)
1atm, according to Chapman–Enskog equation, molecular diffusivity of CO–CO$_2$ is worked out at $1.994 \times 10^{-4} \text{m}^2/\text{s}$.\(^9\) Szekely et al. thought Chapman–Enskog equation still can be used for gas diffusion in the porous solids,\(^{12}\) but then effective diffusivity ($D_e$) should substitute for diffusivity. The effective diffusivity was calculated by the following equation:

$$D_e = (\varepsilon / \tau)D \quad \text{(2)}$$

Where $\varepsilon$ is the porosity and $\tau$ is the tortuosity of porous solids. The porosity may be measured by using test method, but the tortuosity cannot be directly measured. Once, someone did the systemic research about the tortuosity of porous solids, introducing the relationship with porosity and tortuosity of porous solids.

$$\tau = 1 / \varepsilon \quad \text{(3)}$$

The author think that the open porosity of pellets influences the diffusivity, so combine formula (1), (2) and (3), during the reduction, the effective diffusivity is defined by the following formula:

$$D_e = (\varepsilon')^2D \quad \text{(4)}$$

Where $\varepsilon'$ is the open porosity of pellet.

According to formula (4), the effective diffusivities of preheated and oxide pellets during the non-coking coal reduction are worked out in Fig. 12. From the curves, it can be seen that the effective diffusivity of oxide pellets is lower than that of preheated pellets due to low open porous volume. And the effective diffusivity of CO–CO$_2$ in preheated pellets is obviously higher than that in oxide pellets, which means the reduction kinetics conditions of preheated pellets are superior to oxide pellets.

5. Conclusions

Preheated pellets and fired oxide pellets made of magnetite concentrate possess huge difference in coal-based reduction behaviors when simulating grate-rotary kiln process, which can be concluded as follows:

1. Preheated pellets possess much better reducibility than fired oxide pellets, 60 min are required for preheated pellets to reach over 90% metallization degree compared to 100 min for fired oxide pellets.

2. Superior reducibility of preheated pellets should be ascribed to their higher effective diffusivity due to higher porosity, agreeing with volumetric reaction model compared to shrinking un-reacted-core model.

3. As fired pellets during reducing at the earlier stage, the compressive strength of preheated pellets drops dramatically. However, compressive strength of preheated pellets climbs quickly and achieves a high value at the end of reduction whereas that of fired pellets is much lower, leading to smooth and intact metallized pellets from reduction of preheated pellets in contrast to more cracks and fractures of metallized pellets from reduction of fired oxide pellets.

4. The preheated pellets possess self-curing function because of the multiple functions of composite binder, eliminate cracks and fractures and keep pellets intact during reducing, depressing reduction degradation and preventing accretion in rotary kiln.

REFERENCES