Relation between Sticking and Metallic Iron Precipitation on the Surface of Fe₂O₃ Particles Reduced by CO in the Fluidized Bed

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The Fe₂O₃ particles (150–224 μm diameter) were reduced in a laboratory fluidized bed with CO–N₂ mixture gas at 700–900°C to investigate the relation between sticking and iron precipitation. As a result, the sticking tended to occur with acceleration of the reduction rate, judging from the fluidization time. The sticking depended strongly on the metallization ratio signifying the probability of iron-iron contact that estimated the contact area of precipitated iron when particles collide together, whereas the reduction degree had indirect influence on it. Many tiny iron grains with the diameter of approximately 20–40 nm were found on the surface of particles by SEM and EDS. According to theory of microcrystal melting point, the grains reached Tammann temperature easily, leading to higher surface energy of iron, producing higher adhesion force among the reduced particles.

KEY WORDS: sticking; fluidized bed; reduction degree; metallization ratio; iron ore.

1. Introduction

The dominating technology for ironmaking is blast-furnace process. Nevertheless, it is strongly dependent upon coke. The price of coke is always rising due to lack of coking coal, resulting in increase of the ironmaking cost.¹,² Many new ironmaking processes as alternatives to the blast furnace have been developed in order to get rid of limit of cokes.³,⁴ Due to no need prior treatment for fine iron ores, uniform temperature in the reactor and excellent heat and mass transport, the fluidized bed had been used as reduction or pre-reduction reactor in many processes.⁵,⁶ However, defluidization due to sticking occurred easily during reduction of fine iron ores in the fluidized bed,⁷–¹² impeding the industrialization of fluidized bed reactors during ironmaking process.

Three different types of sticking were recognized by many former investigations on reduction of fine iron ore in the fluidized bed.¹⁰–¹³ The first type of sticking was caused by freshly precipitated iron with high surface energy. The iron resulted in high adhesion force between reduced iron ore particles. S. Hayashi and Y. Iguchi¹⁴ further studied on relation between sulfur pressure and sticking of fine iron ores in fluidized bed reduction. The iron saturated by atoms of sulfur had high surface energy, tending to cause sticking. The second kind of sticking appeared when some iron whiskers precipitated on the particle surface, being initiated by the contact of the whisker that hooked mechanically the particles together. J. F. Gransden and J. S. Sheasby¹⁵ also reported that the iron whisker precipitated on the surface of particle permitting iron-iron contact and thereby causing sticking. And the iron whisker was one type of morphology of precipitated iron with high surface energy.¹⁶ The third type of sticking occurred accompanying with a liquid phase within the overheated zone, which was stimulated by presence of gangue, because there was a build up of low melting eutectic phase (CaO–SiO₂–FeO) that stucked together in an iron ore particle. R. Degel⁷ reported that the ores had a strong sticking tendency at temperature above 810°C. When temperature increased, some compounds of the iron ore started to soften and melt.

Since the iron ore has complicated chemical composition, leading many factors affecting sticking of ore particles to entangle together, it was difficult to clarify the sticking mechanism of each factor. To simplify the chemical composition of iron ores, chemical grade Fe₂O₃ particles were selected as materials for reduction in the fluidized bed. The most former researches mentioned above indicated the sticking was associated with the precipitated iron, but the relation between sticking and the reduction degree found by them was unreasonable, because the reduction degree could not describe exactly the quantity of precipitated iron. Moreover, T. Mikami et al.¹⁶ reported the sticking was the result of sintering of metallic iron. However, they discussed defluidization resulted from neck growth by keeping the contact of particles for one hour. Obviously, the time of particles remaining in the fluidized bed was far less than one hour. Based on these former findings, this paper discussed the relation between sticking and precipitated iron by metallization ratio, and explored the sticking mechanism of precipitated iron by analysis of the surface energy of iron.
2. Experimental

2.1. Material Preparation

In this study, Fe₂O₃ particles were used for experiment. Reagent grade Fe₂O₃ powder (≥ 99%) was pressed into tablets with 150 MPa. The tablets were sintered in a crucible furnace at 1 200°C for 168 h to grow the large grain. The sintered tablets were crushed and screened between 150–224 μm, and then the particles were used in the following experiment. Figure 1 illustrates the XRD patterns of particles before and after sintering. The main chemical composition of materials after above preparation is still Fe₂O₃. The surface morphology of particles after preparation is dense and angular, as shown in Fig. 2.

2.2. Experimental Procedure

The schematic diagram of the experimental setup is shown in Fig. 3. The electrical heating shell is a transparent furnace providing the observation of the fluidized state during reduction. The fluidized bed reactor is a silica tube (Φ = 30 mm) with a fritted silica distributor plate, and it allows gas flow into reactor from the bottom of the tube. The temperature of furnace and samples are monitored by the thermocouple.

Batches of 50 g Fe₂O₃ particles after preparation were put into the fluidized bed reactor, and then fluidized by N₂ with flow rate of 3 L/min. The fluidized bed was heated to the expected temperature (700°C, 800°C, 900°C). After maintaining the system at the expected temperature for a few minutes to keep N₂ wash the system free from the air, N₂ was switched to the reduction mixture gas (CO+N₂) with the same flow rate. Once the complete defluidization occurred and the pressure was steady, the reduction mixture gas was switched to the pure N₂ with flow rate of 1 L/min immediately, as shown in Fig. 4. The atmosphere was kept until the temperature of the particles dropped to room temperature. Finally, the particles were obtained from the reactor and put in the dryer for standby.

After each experiment, the blank experiment was carried out to test the blank pressure. The pressure drop of the powder layer was equal to the experiment pressure minus the blank pressure.

2.3. Determination of the Sticking

The sticking during reduction in the fluidized bed was determined by combining the abrupt change of pressure drop though bed with observation of the state of fluidization. Fig. 4 illustrates the variation of the pressure drop with reduction time.
reduction time reduced by CO–N₂ mixture gas (CO 2 L/min, N₂ 1 L/min) at 700°C. At initial stage of reduction, the pressure drop was steady and the state of particles was in fluidization. For a while, the pressure drop fell sharply and the state of particles became in defluidization. The fluidization time (tf) is defined from the start of reduction gas flowed into reactor to occurrence of sticking judged by the start of the dramatic drop of the pressure drop. As seen in Fig. 4, the time corresponding to the intersection of two tangent lines is the fluidization time. The shorter fluidization time indicated that the sticking much tended to happen.

2.4. Characterizations

The reduction degree was calculated by the following equation

\[ R = \frac{0.5Fe^{2+} + 1.5Fe^0}{1.5TFe} \] ........................ (1)

And the metallization ratio was calculated by the following equation

\[ M = \frac{Fe^0}{TFe} \] ................................. (2)

where TFe, Fe^{2+} and Fe^0 are the quantity of the total iron, the ferrous iron and the metallic iron respectively, which are measured by chemical analytical methods according to GB/T 6730.5-2007, GB 6730.8-86 and GB 6730.6-86.

The phase of the particles was analyzed by X-ray diffraction (X’Pert Pro, MPDalytical, Cu target, 2θ: 10–90°). The morphology of reduced particles was observed by field-emission scanning electron microscopy (SEM) (JEO JSM 6700F). Polarization microscope (Laitz, DMRX) was used to observe optical micrographs of cuts through reduced particles.

3. Results and Discussion

3.1. Variation of Fluidization Time and Reduction Degree

In order to discuss the relation between sticking and the quantity of precipitated iron, fluidization time and reduction degree were examined firstly. The variation of fluidization time and reduction degree with reduction temperature at CO–N₂ mixture gas atmosphere (CO 2 L/min, N₂ 1 L/min) is showed in Fig. 5. The fluidization time at 700°C, 800°C, and 900°C is 619 s, 595 s and 475 s respectively. But the reduction degree had small increases within 34.17%–35.35%.

Figure 6 illustrates the variation of fluidization time and the reduction degree with the concentration of CO at 900°C. The fluidization time is 840 s, 475 s and 372 s under 33%CO mixture gas, 67%CO mixture gas and 100%CO gas, respectively. And the reduction degree increases from 34.51% to 39.38% with the increase of concentration of CO.

Earlier researchers\(^{11,12,14}\) proved that the sticking occurred when the reduction degree reached above 30%, those were in agree with the results shown in Figs. 5 and 6. Increasing the reduction temperature resulted in higher reaction rate, therefore, shortening the fluidization time. Increasing concentration of CO improved diffusion of the gaseous reactants through the pores of the particle to the internal sur-

face, leading to decrease of the fluidization time. The result indicated the sticking tended to occur with acceleration of the reduction rate.

Due to the same influence of the reduction time on the reduction degree and the metallization ratio, it was ignored when the two parameters were compared. For this reason, the effects of reduction conditions were significant. The reduction degree varied slightly with reduction conditions, especially, the reduction degrees at 800°C and 900°C were almost steady in Fig. 5. The reason was that the effect of temperature on the reduction rate was less strong above 700°C.\(^{17}\) And the rate of reduction from Fe₂O₃ to Fe₁–xO was fast at high temperature,\(^{18}\) weakening the effect of concentration of CO on the reduction degree. Therefore, the reduction degree increased slightly with increase of temperature and concentration of CO when sticking happened.

3.2. Variation of Metallization Ratio

For the sake of clarifying the relationship between sticking and the quantity of precipitated iron, the phase composition of reduced particles was studied. Figure 7 illustrates the XRD patterns of the particles reduced by CO–N₂ mixture gas (CO 2 L/min, N₂ 1 L/min) at various temperatures. The samples reduced at 700°C and 800°C contain magnetite, wustite and ferrum. The sample reduced at 900°C only
contains wustite and ferrum. The diffraction peaks of ferrum strengthened with increasing temperature, but those at 800°C and 900°C varied slightly. Figure 8 shows the XRD patterns of the particles reduced by various gas compositions at 900°C. All samples only contain wustite and ferrum. The diffraction peaks of ferrum obviously strengthened with increasing concentration of CO, which was in accord with the fluidization time changed with CO concentration. Therefore, it was inferred that the sticking depended upon the amount of precipitated iron.

The metallization ratio of particles was tested in order to study exactly the relation between sticking and the quantity of precipitated iron. The variation of metallization ratio with reduction temperature is illustrated in Fig. 9. The metallization ratios of particles reduced at 700°C, 800°C and 900°C reach 8.93%, 12.97% and 12.76% respectively. Figure 10 illustrates the variation of metallization ratio with concentration of CO gas at 900°C. The metallization ratios of particles reduced under three different gases reach 9.47%, 12.76% and 18.48% respectively.

The variation of metallization ratio was in consistent with that of reduction degree, but there also was quite difference. The reason was that the metallization ratio only depended upon the reduction from Fe$_{1-x}$O to Fe. And the reduction from Fe$_2$O$_3$ to Fe$_{1-x}$O was faster than that from Fe$_{1-x}$O to Fe, therefore the latter was the controlling step of reduction of the iron oxide. The reduction from Fe$_{1-x}$O to Fe in the fluidized bed reactor must proceed through the following steps:

1. Transport of the gaseous reactants (CO) from the bubble phase of the fluidized bed into the emulsion phase.
2. Transport of the gaseous reactants from the emulsion phase to the external surface of the Fe$_{1-x}$O particle.
3. Diffusion of the gaseous reactants through the pores of the particle to the internal surface.
4. Reduction of the iron oxide
   \[
   \text{CO} + \text{O}^2- \rightarrow \text{CO}_2 + 2e^- \\
   \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}
   \]
5. Diffusion of products (CO$_2$) from the pores of the particles to the external surface.
6. Transport of products from the external surface into the emulsion phase.
7. Transport of products from the emulsion phase into the bubble phase of the fluidized bed.
Steps (1), (2), (6) and (7) were not the rate controlling step as the gaseous flow rate was quite fast in the fluidized bed. The reaction rate of reduction from Fe$_{1-x}$O to Fe accelerated with increasing reduction temperature due to the intensification of step (4). At the same condition, the metallization ratio of particles at 800°C as sticking occurred was 12.97%, more than that at 700°C. In addition, the reduction rate from Fe$_{1-x}$O to Fe accelerated with increasing concentration of CO due to the intensification of steps (3) and (5). Consequently, the higher reduction temperature and concentration of CO, the more precipitated metallic iron when sticking occurred.

3.3. Evolution of Reduction Degree and Metallization Ratio with Time

To further discuss the influence of reduction degree and metallization ratio on the sticking, their evolution with time was studied. Figure 11 shows the variation during reduction of particles by CO (2.67 L/min) at 900°C. The reduction degree and metallization ratio increase with reduction time. The variation of reduction degree before sticking performs linearity. After sticking, the reduction rate slightly decreases. The metallization ratios at 30 s and 60 s before sticking are quite low, even less than 3%. But, it reaches 10.88% when sticking happens. After sticking, the rate slightly decreases.

The variation rate of the reduction degree and the metallization ratio decreased after sticking in that sticking caused the gaseous reactants flowed through channels of powder layer, hindering the gas-solid contact. The variation rate of the reduction degree was constant before sticking, but the metallization ratio increased rapidly when sticking occurred. From the result, the sticking tended to occur with increasing metallization ratio. And J. F. Gransden and J. S. Sheasby also reported that sticking of particles in the fluidized bed occurred whenever iron contacted each other. Therefore, the sticking depended strongly on the metallization ratio.

For getting detailed knowledge about relation between the sticking and the metallization ratio, optical micrographs were made of cuts through reduced particles. A cut through a particles reduced by CO at 800°C where sticking occurred is shown in Fig. 12. There are a high amount of pores throughout the whole particle. The precipitated iron is both on the surface and inside of the particle. Although the material particle was dense through the preparation process above mentioned, its density was lower than that of raw iron ore. The pore was easily formed in the material particle, which let reduction gas into the particle, resulting in the precipitation of the metallic iron inside of the particle. The similar phenomenon appeared during reduction of iron ores with H$_2$, which reported by Habermann et al. The iron layer with covering the particle was not formed, but the metallic iron with shape of the grain precipitated on the surface. The result indicated that the metallization ratio signified the probability of iron-iron contact, thereby estimating the contact area of precipitated iron when particles collide together.

3.4. Mechanism of Sticking Caused by Precipitated Iron

In order to discuss the mechanism of sticking caused by precipitated iron, the particles in Fig. 7 (700°C) were fluidized by N$_2$ with gas flow rate of 2 L/min at programmed temperature to simulate the situation of the precipitated iron after collision of the particles. The variation of pressure with temperature is illustrated in Fig. 13. The pressure increases with increasing temperature. There is a small change of

![Fig. 11. Variations of reduction degree and metallization ratio with time.](image1)

![Fig. 12. Optical micrograph of a cut through a particle reduced by CO at 800°C where sticking occurred.](image2)

![Fig. 13. Variation of pressure with temperature during the fluidization of particles by N$_2$.](image3)
pressure curve at 320°C, and the state of particles is observed from packed bed to fluidized bed. A abrupt drop of pressure curve occurs at 500°C, and the state of particles transforms from fluidization to defluidization. The pressure rises rapidly at 650°C, and the reflooding is observed. The first change of pressure curve was caused by critical fluidized state that removed the friction forces among particles, resulting in slight drop. The second change of pressure curve occurred due to the enlargement of surface energy of particles at high temperature, leading to sticking. The shear force of gas slightly increased with temperature due to the swelling of gas, therefore the sticking was destroyed and the cohered particles fluidized again. The third change of pressure curve was just the point of reflooding.

As shown in Fig. 14(a), there are white tiny grains with diameter of 20–40 nm on the surface of reduced particles and the element of the grain detected by EDS is metallic iron. According to theory of microcrystalline melting point reported by Kelvin, the melting point of microcrystal drops with decreasing of microcrystalline diameter and the relation can be expressed as:

\[
\ln \frac{T_{m}}{T_{s}} = -\frac{2M\gamma}{\rho\Delta H_f r}
\]

where \(T_m\) and \(T_s\) are the melting temperatures of macrocrystal and microcrystal with diameter of r respectively, \(M\) is molecular mass of the crystal, \(\gamma\) is crystalline surface tension, \(\rho\) is crystalline density, \(\Delta H_f\) is crystalline fusion heat and \(r\) is microcrystalline radius.

The starting temperature of solid-phase reaction was far below the fusion temperature of the reactant. It was defined as Tammann temperature (\(T_s\)). At the temperature, the surface energy of the crystal increased dramatically as the lattice vacancies were not fixed anymore and the solid point unit became obviously active. There was certain relation between Tammann temperature of the material and its melting temperature. For metal material, \(T_s\) were 0.3–0.4 \(T_m\). S. Golunski reported that Tammann temperature of iron was 630°C. According Eq. (3), the relation between Tammann temperature of macrocrystal and microcrystal can be expressed as:

\[
\ln \frac{T_{s_{(m)}}}{T_{s_{(r)}}} = -\frac{2M\gamma}{\rho\Delta H_f r}
\]

where \(T_s\) and \(T_{s_{(r)}}\) are Tammann temperatures of macrocrystal and microcrystal with diameter of r respectively. Therefore, Tammann temperature of the tiny iron grain with diameter of 20–40 nm was 503–564°C by calculating with Eq. (4). The value corresponds with the defluidization temperature (500°C) in Fig. 13. As a result, the precipitated iron grain on the surface of particles approached its Tammann temperature, at which the surface energy of the grain eminently increased and that made particles stick.

However, in Fig. 11, there was no sticking at 900°C when particles were reduced for 120 s and the metallization ratio reached 2.31%. There was small contact area of precipitated iron due to few tiny iron grains, which led to low adhesion energy among particles. The result proved the sticking needed large quantities of precipitated metallic iron to provide enough contact area of precipitated iron. That was the reason the sticking tended to occur with increasing metallization ratio.

From above results, the sticking depended upon the temperature and the quantity of the tiny iron grain. The schematic diagram of the mechanism of sticking caused by precipitated iron is illustrated in Fig. 15. The gray sheet means the local grain of Fe_{1-x}O and the white bulge is the tiny iron grain. As shown in Fig. 15(a), if there are many tiny iron grains precipitated on the surface of the reduced particle but the temperature is below Tammann temperature of the iron grain, the reduced particles separate again after collision. Due to lower surface energy of the tiny iron grain at low temperature, there was too low adhesion force among particles to stick together. It was the reason that no sticking occurred at low temperature. As shown in Fig. 15(b), as the temperature is above Tammann temperature but few tiny iron grains are precipitated on the surface of the reduced
particle, the reduced particles separate again after collision. Although the surface energy of the tiny iron grain was high at the temperature, the quantity of the iron grain was few, thus there was too small area of contact among particles to stick together. That was proved in Fig. 11. As shown in Fig. 15(c), when the temperature is above Tammann temperature and many tiny iron grains are precipitated on the surface of the reduced particle, the reduced particles stick together after collision due to enough adhesion force and area of contact among particles. The result in Figs. 9 and 10 proved the case.

4. Conclusions

The relation between reduction and sticking were studied by reduction of Fe$_2$O$_3$ particle with CO in the fluidized bed. As a result, the sticking tended to preferred with acceleration of the reduction rate. And the metallization ratio was estimated the contact area of precipitated iron, therefore, the sticking depended strongly on it.

The mechanism of sticking caused by precipitated iron was discussed by the fluidization of reduced particles by N$_2$. The result showed many tiny iron grains with the diameter of approximately 20–40 nm were on the surface of particles. The grains with higher surface energy due to reaching Tammann temperature resulted in higher adhesion force among the reduced particles.

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