Characterization of Precipitated Carbon by XPS and Its Prevention Mechanism of Sticking during Reduction of Fe_2O_3 Particles in the Fluidized Bed

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The Fe_2O_3 particles with the diameter between 74 and 150 μm were pre-reduced with CO at 923 K to precipitate the carbon on the surface. Then the particles were reduced by CO at 1173 K in the fluidized bed for examining the efficiency of the precipitated carbon for preventing the sticking. The result showed that the sticking of particles with high metallization ratio could be retarded or prevented by the precipitated carbon. For clarifying the prevention mechanism of the sticking, the carbon in different states was characterized by X-ray Photoelectron Spectroscopy (XPS) and its effects on sticking were discussed. The carbon on the surface was divided into two states, the graphitic carbon and the carbon in Fe_3C . On account of the sticking of Fe_3C at approximately 1054 K and the sticking of the sponge iron at the micron scale, the structural change of the precipitated iron by the carburization and the formation of Fe_3C only retard the sticking. Therefore, the prevention of the sticking at 1173 K was attributed to the graphitic carbon. Due to the formation of metallic iron layer avoiding the consumption of the carbon and the formation of Fe_3C restraining the dissolution of the graphitic carbon, the graphitic carbon accumulated on the surface of the particles, resulted in $n_{\text{C}}/n_{\text{Fe}}$ above 1.0, so that Fe_3C and the metallic iron was coated by the graphitic carbon to block their contact among the particles.

KEY WORDS: fluidized bed; Fe_2O_3 particles; prevention of sticking; pre-reduction; graphitic carbon; Fe_3C .

1. Introduction

The fluidized bed with advantages of direct utilization of iron ore fines, no dependence on coke, excellent heat and mass transfer was selected as reactor for reduction or pre-reduction of iron ores as an alternative to blast furnace.^{1–4)} However, the industrialized development of the fluidized bed in iron-making was limited,^{5–7)} which was mainly attributed to the defluidization resulted from sticking among iron ore particles.^{8–11)}

To prevent sticking problem during reduction of iron ores in the fluidized bed, some methods were proposed by previous researchers. Low reduction temperature that led to small adhesive force among iron ore fines and high gas velocity that produced high momentum of particles were useful for suppressing sticking.^{9–14)} However, these methods resulted in low reduction rate of iron ores and utilization ratio of the reduction gas,¹⁴⁾ increasing the cost of production. Otherwise, the iron ore fines with additions of CaO, MgO and Al_2O_3 showed the sticking could be avoided or decreased.^{8–10)} While, the coating methods of powder, solution and slurry were by means of mechanical mixing, lead-

ing to the non-uniform distribution of additives on the surface of iron ore fines that lowered the prevention efficiency for sticking. Moreover, the method was more or less difficult in operation.

Compared with above methods, the carbon precipitation to prevent sticking was an economic, convenient and efficient method.^{15,16)} The carbon was coated on the surface of iron ore fines by the Boudouard reaction or methane decomposition in the pre-reduction reactor, leading to uniform distribution of carbon and high strength.^{16,17)} The prevention mechanism of sticking proposed in previous works was that the carbon on the surface blocked the contact of metallic iron among the particles or the carbon dissolved in iron changed the morphology of subsequent precipitated iron,^{17,18)} based on the knowledge that sticking was caused by the iron whisker. However, Y. W. Zhong *et al.*¹⁹⁾ and J. H. Shao *et al.*²⁰⁾ reported that the pure iron fines without the iron whisker occurred sticking, indicating that the high surface energy of iron at high temperature was the crucial reason for occurrence of sticking. Therefore, the prevention mechanism of sticking by the precipitated carbon was necessary to study further. In addition, the state of the carbon on the surface of particles was not reported in previous papers, which was helpful for clarifying the prevention mechanism of sticking.

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To simplify the chemical composition of iron ores, chemical grade Fe_2O_3 particles were selected as the model material for reduction with CO in the fluidized bed. The carbon precipitated on the surface of particles by the reaction during pre-reduction at 923 K, and the pre-reduction particles were fluidized reduction at 1 173 K to examine the efficiency of precipitated carbon for preventing sticking. The carbon on the surface of particles in different states was characterized by XPS, and the prevention mechanism of sticking by the precipitated carbon was discussed in the final part.

2. Experimental

2.1. Experimental Procedure

The experimental apparatus and preparation process of Fe_2O_3 particles was reported in previous paper.²¹⁾ The pre-reduction process was as follows. Batches of 30 g Fe_2O_3 particles with the diameter between 74 and 150 μm were fed into the fluidized bed reactor, and then fluidized with N_2 at a flow rate of 3 L/min. The fluidized bed was heated to 923 K. After maintaining the system at 923 K for a few minutes to keep N_2 wash the system free from air, N_2 was switched to 3 L/min CO. When the specified time reached, the CO gas was switched back to the pure N_2 at a flow rate of 1 L/min immediately. The atmosphere was kept until the temperature of the particles dropped to room temperature. The final reduction was as shown below. The empty fluidized bed was heated to 1 173 K with 3 L/min N_2 . Then 20 g particles obtained from the pre-reduction process were fed into the fluidized bed reactor and the N_2 gas was switched to 3 L/min CO immediately. Once the complete defluidization occurred and the pressure was steady, the CO gas was switched back to the pure N_2 at a flow rate of 1 L/min immediately. And the atmosphere was kept until the temperature of the particles dropped to room temperature. If the defluidization not occurred, the same operation was performed when the reduction time reached 30 min. All the samples after reduction were kept in the dryer for further characterization.

2.2. Characterizations

The metallization ratio was calculated by the following equation

$$M = \frac{Fe^0}{TFe} \dots\dots\dots (1)$$

where TFe and Fe^0 are the quantity of the total iron and the metallic iron respectively. The total carbon content of particles was examined by the Infrared Carbon-Sulfur Analyzer (LECO, CS-344). X-ray Photoelectron Spectroscopy (XPS) (Shimadzu International, AXIS Ultra DLD) was used to analyze the surface of particles. The $\text{Al } K\alpha$ line was used for the X-ray source. The pressure of the analysis chamber during measurement was 6.67×10^{-7} Pa. The particles were examined with environmental scanning electron microscope (ESEM) (FEI, Quanta 250) to study their surface structure, while the internal structure was examined with an optical light microscope (LM) (Carl Zeiss, Axio Imager A1). The phase of the particles was analyzed by X-ray diffraction (X'Pert Pro, MPDalytical, Cu target, 2θ : 10–90°).

3. Results

The efficiency of precipitated carbon for preventing sticking was tested by the fluidized state of the pre-reduced particles at high temperature. **Figure 1** shows the pressure variation of particles with different pre-reduction time during fluidized reduction with CO at 1 173 K. The fluidized time (t_f) of the particles with the pre-reduction time of 10 min and 30 min are 73 s and 149 s, respectively. The t_f increases with pre-reduction time, meaning the sticking is retarded by the pre-reduction. When the pre-reduction time is 45 min or 60 min, the defluidization never occurs during the reduction for 30 min, indicating the sticking is prevented to happen. The increase of the pressure in last two cases might be caused by the precipitated carbon that entered the exhaust pipe with gas and formed slight blockage. The results showed that the pre-reduction at 923 K could retard or prevent the sticking at 1 173 K.

The metallization ratio of particles with the pre-reduction

Fig. 1. Pressure variation of particles with different pre-reduction time at 1 173 K.

and the final reduction are shown in **Fig. 2**. In the pre-reduction process, the metallization ratio of particles increases from 10.57% to 38.22% with pre-reduction time from 10 min to 60 min. After the final reduction, the metallization ratios of particles with pre-reduction time from 10 min to 60 min increase from 56.21% to 78.64%. The variation was depended on the reaction time. It was noted that the particles with the metallization ratio of 72.33% or 78.64% did not occur sticking at 1173 K.

Figure 3 illustrates the carbon content of particles with the pre-reduction and the final reduction. The carbon content of particles with the pre-reduction time of 10 min and 15 min are 3.64% and 3.61% respectively. With increasing the pre-reduction time from 20 min to 60 min, the carbon content increases from 5.32% to 19.47%. After the final reduction, the carbon content of particles with the pre-reduction time of 10 min, 15 min, 20 min and 30 min are 1.37%, 2.01%, 3.08% and 6.17% respectively, which are all lower than that before the final reduction. However, the carbon content of particles with the pre-reduction time of 45 min and 60 min without sticking are 16.80% and 22.67% respectively, which are all higher than that before the final reduction. These results strongly suggested that the prevention of sticking rested in the variation of the carbon content of particles.

In above all, the sticking was retarded or prevented at high metallization ratio and temperature on account of the carbon precipitation through the pre-reduction with CO.

Fig. 2. Metallization ratio of particles before and after final reduction.

Fig. 3. Carbon content of particles before and after final reduction.

4. Discussion

4.1. The Characterization of the Carbon in Different States

To understand the sticking prevention mechanism by the precipitated carbon, the state of the carbon needed to be clarified firstly. The XPS analysis was used to identify the different states of carbon on the surface of particles by the study for C 1s core level spectra. Each XPS curve was subjected to peak fitting using XPSPEAK 4.1 and presented in **Fig. 4**. The carbon is in two states, such as the graphitic carbon with the binding energy of 284.6 eV and the carbon in Fe₃C with the binding energy of 283.7 eV.²²⁾ The proportion of the carbon in different states is calculated by integrating the peak area, which is also illustrated in **Fig. 4**. Combining **Figs. 3** and **4**, the content of the carbon in different states is calculated and the result is shown in **Fig. 5**. In the particles with the pre-reduction time of 30 min, the content of the graphitic carbon before and after the final reduction are 3.42% and 2.79% respectively, and the content of the carbon in Fe₃C are 5.35% and 3.38% respectively. For the pre-reduction time of 60 min, the content of the graphitic carbon are 7.39% and 9.91% respectively, and the content of the carbon in Fe₃C are 12.07% and 12.76% respectively. The variation of the carbon content would be discussed in 4.2 below. Above results indicated that the most of the carbon was the carbon in Fe₃C.

During the pre-reduction process, the stepwise reduction reactions from Fe₂O₃ to Fe by CO above 843 K were as follows:⁹⁾

Besides the above mentioned reactions, the Boudouard reaction was possible to occur:²³⁾

The reaction would be promoted by the presence of metallic iron. Due to the effect of atomic force field on the surface of iron, the bond between carbon atom and oxygen atom weakened, leading to the decomposition of CO to form CO₂ and the carbon atom that connected with the iron atom.¹⁷⁾ And the carbon produced from Reaction (5) would dissolve in the precipitated iron to form Fe₃C as Reaction (6).²³⁾

Due to large amount of metallic iron precipitated from the particles, most carbon was dissolved in the iron to form Fe₃C. This was the reason of more carbon in Fe₃C than the graphitic carbon.

4.2. Consumption and Accumulation of the Carbon

In **Fig. 3**, after the final reduction, the carbon content with the pre-reduction time of 30 min or less is lower than that before the final reduction, which indicated that the carbon produced from the pre-reduction was consumed at high temperature. To study the consumption of the carbon, the Fe₂O₃

Fig. 4. XPS spectra of C 1s in particles.

Fig. 5. Content of carbon in different states.

Table 1. Variations of carbon content and metallization ratio of particles before and after temperature rise.

	Before temperature rise	after temperature rise
Carbon content/mass%	4.60	0.056
Metallization ratio/%	19.48	29.18

particles with the diameter between 150 and 224 μm were pre-reduced for 10 min with 3 L/min CO at 923 K for obtaining the particles with the precipitated carbon on them, then the gas switched to N_2 at the same flow rate and the temperature rose from 923 K to 1173 K with the rate of 8.3 K/min. The variations of the carbon content and the metallization ratio of the particles before and after the temperature rise are shown in **Table 1**. The carbon content of the particles before the temperature rise is 4.60%, while the carbon content after the temperature rise is 0.056%, which reveals that the carbon is consumed during the process of the temperature rise. The metallization ratio of particles before and after the temperature rise are 19.48% and

Fig. 6. Analysis of free energy for three reactions.

29.18% respectively, which indicates that the iron oxide is reduced during the process of the temperature rise. On account of the nitrogen atmosphere, the reduction of iron oxide was caused by the carbon produced from the pre-reduction.

The carbon in different states reacted with FeO as follows:

Many researches^{24–26)} reported the decomposition of Fe_3C as follows:

The thermodynamic analysis of above three reactions was performed and the free energy is shown in **Fig. 6**. Above 1000 K, the reaction (7) and (8) are more possible than the reaction (9). In addition, the reaction (9) resulted in the increase of the metallization ratio but not the decrease of the

Fig. 7. Cross sections of the particles with pre-reduction time of 15 min (a), 30 min (b), 45 min (c) and 60 min (d) before final reduction.

carbon content. In Fig. 5, the content of the graphitic carbon and the carbon in Fe_3C with the pre-reduction of 30 min both decreased after the final reduction, indicating that Reaction (7) and (8) proceeded during the final reduction. Therefore, the decrease of the carbon content resulted from the reaction between the carbon atom and the oxygen atom provided by the iron oxide on the surface.

In Fig. 3, the carbon content with pre-reduction time of 45 min and 60 min after the final reduction is higher than that before the final reduction, which is opposite to these with pre-reduction time of 30 min or less. Therefore, the distribution of the metallic iron and the iron oxide were study to discuss the different variation of the carbon content. **Figure 7** shows the cross sections of particles with different pre-reduction time before the final reduction. For 15 min, the metallic iron with grain shape is on the surface and there is the iron oxide around it, resulted in the opportunity of reaction between the iron oxide and the graphitic carbon or Fe_3C . The metallic iron increases on the surface with the pre-reduction time and the iron layer is formed on the surface of particles with the pre-reduction time of 60 min. Due to the absence of the iron oxide on the surface, the Reaction (7) and (8) were difficult to happen, which lead to the accumulation of the graphitic carbon and Fe_3C . This was the reason that the carbon content with the pre-reduction time of 45 min and 60 min increased after the final reduction in Fig. 3. In the iron layer, when the dissolved carbon was saturated, the content of Fe_3C was steady and the content of the graphitic carbon increased obviously, resulted from the precipitation of the graphitic carbon by Reaction (5) and the formation of Fe_3C layer restraining the dissolution of the graphitic carbon through Reaction (6). Therefore, the increase of the carbon content with the pre-reduction time of 45 min and 60 min after the final reduction was attributable mainly to the increase of the graphitic carbon.

Fig. 8. Pressure variations of pure iron particles under different pretreatment with temperature.

4.3. Effect of Fe_3C and Graphitic Carbon on Sticking

Based on the results in Fig. 4, there was a great deal of Fe_3C in the particles. Therefore, the influence of Fe_3C on the sticking must be made clear firstly to understand the prevention mechanism of sticking by the precipitated carbon. For this purpose, the pure iron particles with the diameter between 74 and 150 μm were pretreated by 2 L/min CO for 90 min at 873 K to form Fe_3C on the particle surface, then CO was switched to N_2 at the same flow rate and the temperature rose from 873 K to 1123 K with the rate of 5 K/min. As the contrast experiment, the same pure iron particles were fluidized by 2 L/min N_2 through the same process. The variations of the pressure during the temperature rise are illustrated in **Fig. 8**. In the early stage, the pressure of the fluidized bed within the particles slowly raise with increasing temperature. When the temperature reaches 1027 K, the pressure of particles under the pretreatment in CO

Fig. 9. XRD patterns of pure iron particles under different pretreatment.

sharply declines and the defluidization occurs. However, the defluidization of the particles under the pretreatment in N_2 happens at 952 K. The result showed that the sticking of the pure iron particles was retarded through the pretreatment in CO, but not avoided.

Figure 9 shows the phase analysis of the particles after the temperature rise by XRD. In the particles under the pretreatment in N_2 , the phase is the metallic iron on account of no reaction occurred during the whole process in nitrogen atmosphere. For the particles under the pretreatment in CO, there is Fe_3C besides the metallic iron. And the formation of Fe_3C lead to the decrease of the metallic iron, thus the diffraction peaks of ferrum in the particles under the pretreatment in CO weakens compared with that in N_2 . Due to the excess of the metallic iron, Reaction (6) was most probable to occur. Therefore, the carbon was almost in the state of Fe_3C .

As mentioned in our preview paper,²¹⁾ when the metal at temperature above Tammann 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, which was the mechanism of sticking for the metal. In general, Tammann temperature equals to 30 to 40 percent of the melting temperature.²⁷⁾ For the metallic iron, the melting temperature and Tammann temperature are 1 808 K and 903 K respectively. In Fig. 8, the defluidization of the pure iron particles happened at 952 K that also was reported by Y. W. Zhong *et al.*¹⁹⁾ and J. H. Shao *et al.*,²⁰⁾ which was mostly consistent with above theory. If Fe_3C was regarded as a specific metal and the relationship between Tammann temperature and the melting temperature of Fe_3C was the same as the metallic iron, its Tammann temperature was 1 054 K based on its melting temperature of 2 110 K. The result in Fig. 8 that the defluidization of the pure iron particles under the pretreatment in CO occurred at 1 027 K certified the deduction. Due to the sticking of Fe_3C at high temperature, the effect of Fe_3C was retardation of sticking. Based on that, the prevention of the sticking in Fig. 1 was attributed to the graphitic carbon.

The occurrence of sticking related to the surface of the particles, thus the surface of particles after the final reduction was analysed by SEM, as shown in **Fig. 10**. In Fig. 10 (a), the particle is without pre-reduction. There are many

Fig. 10. SEM analysis of the surface of the final reduced particles without pre-reduction (a) and with pre-reduction time of 30 min (b) and 60 min (c).

fine iron grain at the nanometer scale precipitated on the surface, which are easy to occur sticking on account of their low Tammann temperature. In Fig. 10(b), there is the sponge iron at the micron scale formed on the surface, resulted from the carburization to inhibit the active growth point of the fine iron grain.¹⁵⁾ Nonetheless, the sticking also occurred at 1 173 K, indicating that the structural change only retarded the sticking, but not completely prevented it. In Fig. 10(c), the surface structure also is the sponge iron. However, as compared with Fig. 10(b), there is the fine powder coating the particles obviously. It was the graphitic carbon formed during the reduction.²⁴⁾ Therefore, the particles coated by the graphitic carbon could prevent the occurrence of sticking.

4.4. The Prevention Mechanism of Sticking by Precipitated Carbon

The sticking was caused by the metallic iron and prevented by the carbon; therefore, the efficiency for preventing sticking was related to the carbon content and the metallic iron content of particles. Combining with Figs. 1, 2 and 3, the variations of n_C/n_{Fe} and the fluidization time with the pre-reduction time are shown in **Fig. 11**. Where n_C is the total molar amount of the carbon as the graphitic carbon and the carbon in Fe_3C . When the Fe_3C layer is formed to

restrain the consumption of the graphitic carbon, the latter accumulates on the surface to block iron-iron contact and prevent the sticking. Therefore, n_C includes the molar amount of the carbon in Fe_3C due to its effect on the sticking prevention. And n_{Fe} is the molar amount of the precipitated metallic iron, including the iron in Fe_3C . The reason is that the precipitated metallic iron is main factor leading to the sticking, and Fe_3C also sticks at higher temperature. n_C/n_{Fe} increases from 0.13 to 0.56 with pre-reduction time from 10 min to 30 min, resulting in the extension of the fluidization time from 73 s to 149 s. For the pre-reduction time of 45 min and 60 min, n_C/n_{Fe} are 1.46 and 1.90 respectively, which are both above 1.0, leading to the fluidization time of 1800 s that equals to the reduction time, indicating that the sticking don't occur. The result showed that the sticking could be restrained by the increase of n_C/n_{Fe} and avoided at n_C/n_{Fe}

above 1.0.

For further understanding the prevention mechanism of sticking by the precipitated carbon, its schematic diagram is shown in Fig. 12. During the pre-reduction at low temperature, CO reduces the iron oxide firstly and then precipitates the carbon with the catalysis of metallic iron by Boudouard reaction. And part of the carbon dissolves in the metallic iron to form Fe_3C , as shown in Figs. 12(a) and 12(b). The content and the state of the carbon were examined in Figs. 3 and 4. Due to low metallization ratio, the metallic iron with grain shape is on the surface and there is the iron oxide around it, as shown in Fig. 12(a) and confirmed in Figs. 7(a) and 7(b). The carbon reacts with the iron oxide at high temperature, resulted in the decrease of the carbon and the increase of the metallic iron on the surface; therefore n_C/n_{Fe} is below 1.0. As shown in Fig. 12(c), the bare metallic iron on the surface is easy to contact among the particles, leading to sticking of the particles.

With increasing pre-reduction time, the metallization ratio increases and the iron oxide decreases, resulted in decrease of consumption of the precipitated carbon at high temperature. Therefore, n_C/n_{Fe} increases with pre-reduction time, as shown in Fig. 11. Once the iron oxide was absent on the surface, the metallic iron layer is formed, which is confirmed in Figs. 7(c) and 7(d). And the dissolved carbon is saturated, resulted in the steady content of Fe_3C and the formation of Fe_3C layer. In this case, the structure of the carbon layer at the external position, the Fe_3C layer at the medial position and the iron layer at the internal position on the surface of the particles is formed, as shown in Fig. 12(b). Due to the formation of metallic iron layer avoiding the consumption of the carbon and the formation of Fe_3C restraining the dissolution of the graphitic carbon, the graphitic carbon is

Fig. 11. Variations of n_C/n_{Fe} and the fluidization time with the pre-reduction time.

Fig. 12. Schematic diagram of the prevention mechanism of sticking by precipitated carbon.

accumulated at high temperature, as shown in Fig. 12(d) and proved in Fig. 5. As a result, n_C/n_{Fe} is above 1.0, leading to coating Fe_3C and the metallic iron by the graphitic carbon to block their contact among the particles and prevented the sticking. That is the prevention mechanism of sticking by the precipitated carbon.

5. Conclusion

The Fe_2O_3 particles with the precipitated carbon produced by the pre-reduction were reduced by CO in the fluidized bed at 1173 K to examine the efficiency of the precipitated carbon for preventing the sticking. The carbon in different states was characterized by XPS and its effects on sticking were discussed for clarifying the prevention mechanism of sticking by the precipitated carbon. The main conclusions can be stated as follows.

(1) Through the carbon precipitation during the pre-reduction at 923 K, the sticking of particles with high metallization ratio at 1173 K could be retarded or prevented.

(2) The carbon produced by the pre-reduction was in two states, such as the graphitic carbon and the carbon in Fe_3C .

(3) The structural change of precipitated iron and the formation of Fe_3C only retarded the sticking. The prevention of the sticking at 1173 K was attributed to the graphitic carbon.

(4) The prevention mechanism of sticking by precipitated carbon was that the graphitic carbon accumulated on the surface of the particles by the formation of metallic iron layer avoiding the consumption of the carbon and the formation of Fe_3C layer restraining the dissolution of the graphitic carbon, resulted in n_C/n_{Fe} above 1.0, so that Fe_3C and the metallic iron was coated by the graphitic carbon to block their contact among the particles.

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