Abnormal Swelling during Reduction of Binder Bonded Iron Ore Pellets with CO–CO₂ Gas Mixtures

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Abnormal swelling during reduction of iron ore pellets with CO–CO₂ gas mixtures was investigated in the temperature range of 700 to 1 000°C. Influence of addition of gaseous sulfur COS at low partial pressures to inlet gas mixtures, CO₂/(CO+CO₂) in inlet gas and temperature as well as kinds of binders such as Portland cement, bentonite and lime on swelling were examined.

When the ratio P_COS/P_CO in inlet reducing gas was lower in 10^{-2} than the equilibrium ratio between iron and iron sulfide, abnormal swelling of pellets was observed for non cement bonded pellets, in particular, giving maximum around 900°C. Cement bonded pellets provided moderate abnormal swelling independently of adding gaseous sulfur to inlet gas mixtures. Their swelling seemed to be caused by gasification of sulfur species present in cement. These results supported our previous findings that the existence of sulfur is essential to the abnormal swelling and the swelling is mostly accompanied with the formation of fibrous irons.

The results are discussed along with previous researches and gas chromatography of sulfur species in exit gas to evaluate the sulfur activity in gas near the reaction front inside cement bonded pellets.

KEY WORDS: abnormal swelling during reduction; cement bonded iron ore pellets; bentonite; lime; CO–CO₂–COS gas mixtures; gaseous sulfur; fibrous iron.

1. Introduction

It is known that volumetric swelling of burdens such as sinter or pellets during reduction leads to degradation or lowering gas permeability through packed beds, makes manufacturing operation impossible, the formation of fibrous irons during metallization causes mainly the abnormal swelling of pellets, and most of such swelling are further promoted by adding appropriate lime, alkali, and gaseous sulfur.

Using iron oxide pellets made of reagents, the authors have previously reported a series of works concerning the abnormal swelling of pellets during reduction with CO–CO₂ or H₂–H₂O gas mixtures and concluded that gaseous sulfur in reducing gas causes a maximum abnormal swelling under the sulfur potentials around one tenth as small as Fe/FeS equilibrium and this swelling occurs together with the formation of fibrous irons, being more favorable under the conditions of moderate reduction rates for both gas mixtures. Moreover, correlation between lime or alkali and gaseous sulfur on abnormal swelling was clarified by the authors.

In this work, in order to apply these findings to industrial cases, iron ore fines were individually mixed with Portland cement, bentonite and lime as binder to be agglomerated into pellets and then they were indurated or cured to improve their crushing strength. Then the swelling behavior during reduction of these pellets with CO–CO₂–COS gas mixtures was investigated in elevated temperatures.

Influence of addition of gaseous sulfur COS at low partial pressures to inlet gas mixtures, CO₂/(CO+CO₂) in inlet gas and temperature on swelling were examined.

Moreover, we tried to examine how sulfur species present not only in gas phase but also in binder or iron ore influence the swelling during reduction and to estimate the sulfur potentials in reducing gas inside a pellet by determining contents of sulfur species in exit gas by means of gas chromatography.

On the basis of these obtained results, the abnormal swelling was discussed together with previous related researches.

2. Experiments

Samarco hematite iron ore was selected as base materials. The chemical compositions are shown in Table 1(a). This ore was crushed and screened between 45 and 75 μm. These fines were individually mixed with some amounts of Portland cement, bentonite (Chemical compositions: Tables 1(b) and 1(c)) and lime as binder and made to five types of pellets after different treatments. These preparation conditions were shown in Table 2. Pellet F was cured with hot steam in air under 60°C for 24 h.

These hematite pellets were single reduced partially on one sage to metallic iron at 700–1 000°C in CO–CO₂–COS gas mixtures (1.0 Nl/min) using the previous thermal-
The addition of traces of COS to these mixtures was prepared by bubbling CO gas into an isothermal liquid sulfur bath (110–150°C) and subsequently flowing the exhausted sulfur bearing CO gas through a column of carbon particles at 1000°C. The amounts of COS in gas mixtures were actually confirmed by means of gas chromatography.

The sulfur activity $a_S$ in reducing gas phase is represented by Eq. (1) relatively to Fe/FeS equilibrium, similarly to previous researches.

$$a_S = \frac{P_{\text{COS}}}{P_{\text{CO}}} \left( \frac{P_{\text{COS}}}{P_{\text{CO}}} \right)_e$$  \hspace{1cm} (1)

From thermodynamical calculation, thermal decomposition of COS can be ignored within 0.05% errors. Influence of the sulfur activity in inlet reducing gas was fundamentally examined in this study. This is because the burdens are subjected to the conditions of iron sulfurization in a blast furnace and no iron sulfurization in most direct reduction furnaces.

The hematite pellets were usually reduced partially until approximately $R_w = 0.50$. Here $R_w$ value is defined as the fractional reduction from wustite (Fe$_{0.92}$O) to iron. Then the reduced pellets were cooled in N$_2$ stream. Volumetric swelling degree $V$ (%) of a pellet after partial reduction can be calculated by Eq. (2) using the pellet radii $r_0$ and $r$ before and after reduction respectively.

$$V = \left( \frac{r}{r_0} \right)^3 - 1 \times 100$$  \hspace{1cm} (2)

Moreover, gas chromatography to evaluate contents of sulfur species in exit gas was carried out and sulfur contents in typical pellets before and after reaction were determined by means of the infrared oxygen combustion.

3. Experimental Results

It is generally known that abnormal swelling is remarkable when fibrous irons appear during reduction. This type of metallic iron expands the distance between individual ore fines to induce abnormal volumetric swelling of pellets. This process always allows direct gas access into the reaction front of wustite grains inside a pellet.

(1) Dependence of Reduction Degree on Swelling

The value $R_w$ is defined as the fractional reduction from wustite to iron, that means metallization degree. It is supposed that the abnormal swelling accompanied with fibrous iron would be almost proportional to the value of $R_w$.

These supposition was satisfied as shown in Fig. 1, where pellets A, B, and F were partially reduced in 80%CO–20%CO$_2$ gas mixtures with $a_S = 0$ or $a_S = 0.10$ at 900°C.

Therefore, the swelling degree $V_{100}$ (%) for complete re-

**Table 1(a).** Chemical compositions of Samarco hematite iron ore [mass %].

|    | Fe  | SiO$_2$ | Al$_2$O$_3$ | P   | S   | CaO  |
|----|-----|---------|-------------|-----|-----|------|
|    | 66.74 | 1.76   | 0.35        | 0.051 | 0.005 | 0.06 |

**Table 1(b).** Chemical compositions of Portland cement [mass %].

|    | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | Na$_2$O | K$_2$O |
|----|---------|-------------|-------------|-----|-----|--------|---------|--------|
|    | 20.99   | 5.50        | 2.61        | 63.85 | 1.58 | 2.32   | 0.32    | 0.39   |

**Table 1(c).** Chemical compositions of Bentonite [mass %].

|    | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | Na$_2$O |
|----|---------|-------------|-------------|-----|-----|--------|---------|
|    | 67.52   | 12.97       | 2.94        | 3.115 | 2.04 | 1.14   | 2.43    |

**Table 2.** Preparation conditions of several kinds of pellets.

| Series Name of pellets | Additives (Binder) | Treatments | Cracking Strength (kg/cm$^3$) |
|------------------------|--------------------|------------|-----------------------------|
| A                      | Nil                | 1000°C, 2hr indurated in air | 3.4 |
| B                      | 4 mass% Cement     | 1000°C, 1hr indurated in air  | 7.7 |
| D                      | 1 mass% Bentonite  | 1000°C, 2hr indurated in air  | 14.3 |
| F                      | 4 mass% Cement     | 600°C, 24hr Cured in air with steam | 6.7 |
| H                      | 1.3 mass% CaO      | 1000°C, 2hr indurated in air  | 16.4 |

Fig. 1. Relation between swelling degree $V$ and fractional reduction $R_w$. © 2003 ISIJ
duction can be defined by Eq. (3) to evaluate the swelling degree obtained for each reaction test.

\[ V_{100} = \frac{V}{R_{W}} \]  

(3)

(2) Influence of Sulfur Activity in Gas \( a_S \) on Swelling

Figure 2 shows influence of sulfur activity in gas \( a_S \) on swelling during reduction at 900°C with 80%CO–20%CO\(_2\) gas mixtures. Pellets A, D, and H did not almost swell for gas conditions without gaseous sulfur except pellet H showing \( V_{100}(\%) = 142 \). However, remarkable abnormal swelling was observed for gas conditions with sulfur activities having \(-1.6 < \log a_S < -0.3\) and maximum swelling for those around \( \log a_S = -0.3 \). The addition of bentonite or lime lessened a little these abnormal swelling. On the other hand, pellets B and F do not almost have sulfur activity dependence of \( V_{100} \) values, giving considerable abnormal swelling of \( V_{100}(\%) = 263–385 \) for pellet B and \( V_{100}(\%) = 129–288 \) for pellet F. These swelling are supposed to be caused by sulfur species derived from cement present in the pellets. This will be discussed in Chap. 4.

(3) Influence of \( \text{CO}_2/(\text{CO}+\text{CO}_2) \) in Inlet Gas on Swelling

Figures 3(a) and 3(b) show influence of \( \text{CO}_2/(\text{CO}+\text{CO}_2) \) ratio in gas on swelling for three types of pellets A, B, and F at 900°C. Where both Fe/FeO phases equilibrate at \( \text{CO}_2/(\text{CO}+\text{CO}_2) = 0.328 \). It was found that most of swelling increased with increasing the ratio, regardless of presence of gaseous sulfur. Particularly, pellet A had a little larger dependence of \( \text{CO}_2/(\text{CO}+\text{CO}_2) \) ratio in inlet gas on swelling for the condition of \( a_S = 0.10 \) (Fig. 3(b)). These results seem to correspond to a previous knowledge that abnormal swelling is preferred for pellets with moderate reduction rates.\(^{1,12,20}\)

On the basis of these results, the gas composition of \( P_{\text{CO}}/P_{\text{CO}_2} = 0.8/0.2 \) was mainly selected in the present work to evaluate the swelling degree obtained for various conditions.

(4) Influence of Temperature on Swelling

Relation between \( V_{100}(\%) \) values and temperature is shown in Fig. 4, where pellets A, B, F and H were reduced under 80%CO–20%CO\(_2\)–COS mixtures having \( a_S = 0 \) (Fig. 4(a)) or \( a_S = 0.10 \) (Fig. 4(b)). Pellet A provided \( V_{100}(\%) < 100 \) % at all temperatures for \( a_S = 0 \) and \( V_{100}(\%) = 732 \) % maximum at 900°C for \( a_S = 0.1 \). The swelling decreased up to \( V_{100} = 155 \) % at 1000°C for \( a_S = 0.1 \).

Pellet B provided \( V_{100} = 569–672 \) % regardless of the presence of COS in inlet gas at 700 and 800°C. These swelling decreased gradually with temperatures, regardless of the presence of COS in inlet gas, giving maximum swelling around 900°C.

Pellet F provided \( V_{100} = 69–259 \) % for all reduction temperatures, regardless of the presence of COS in inlet gas, giving maximum swelling around 800 and 900°C.

Pellet H provided \( V_{100} = 142–221 \) % for \( a_S = 0 \) around 800 and 900°C and \( V_{100} = 463 \) % maximum swelling for \( a_S = 0.1 \) at 900°C.
For pellets A and H with the presence of COS in inlet gas, it was found that their maximum swelling was observed around 900°C, analogous to previous researches.\(^{6,7,12,21}\) In case of \(a_{S}/H_{11005}^{0}=0.1\), addition of CaO into a pellet lessened swelling a little than pellet A.

(5) Macro and Micro Structures in Pellets

Figure 5 shows macro and microscopic structures in pellets before and after reduction. Much microscopic fine fibrous irons were observed when macroscopic abnormal swelling took place. The formation of finer fibrous irons made these swelling more remarkable.

4. Discussion

4.1. Influence of Sulfur Potential on Swelling

As seen in Fig. 2, abnormal swelling for pellets A, D, and H was remarkable when the sulfur activities in inlet gas \(a_{S}\) were in the ranges of \(log a_{S}/H_{11005}^{0}=0.1–0.2\) obtained in our previous researches.\(^{6,7,12}\) Therefore, gas chromatography was done to determine the content of sulfur species COS in exit gas. The results proved that both pellets B and F have the activity around \(a_{S}/H_{11005}^{0}=2\) at 800 and 900°C in the reaction front during metallization which were evaluated by using reduction rates of wustite to iron \(V_{W}\) (g/cm\(^2\)s) defined as oxygen removal per unit area and time, as shown in Table 3 and later Fig. 7. These swelling are supposed to be caused by sulfur species derived from cement present in the pellets.

Moreover, a relation between \(a_{S}\) values in inlet gas and sulfur contents after reduction was obtained as shown in Fig. 6, where both seem to have a relation. These sulfur contents will be mostly driven from sulfur species chemisorbed on the surface of metallic iron.

4.2. Influence of Gas Composition CO\(_2\)/(CO + CO\(_2\)) on Swelling

It is generally known that the reduction of wustite to iron proceeds along with both processes of the chemical reaction on the surface of wustite with gas and the diffusion of iron cation in wustite.\(^{22}\)
Nicolle et al.\textsuperscript{20} have explained variations of whisker, sponge, and plain iron morphology produced in CO–CO\textsubscript{2} gas by introducing the relative resistances for forementioned both processes and the surface property of wustite. According to their idea, less \( P_{\text{CO}_2}/P_{\text{CO}} \) in reducing gas leads to less fibrous irons because the latter process controls the reduction rate and reversely, larger \( P_{\text{CO}_2}/P_{\text{CO}} \) in reducing gas leads to fibrous irons because the former process controls it. Moreover, they mentioned that the condition of larger \( P_{\text{CO}_2}/P_{\text{CO}} \) near Fe/FeO equilibrium makes fibrous irons lessen due to further sintering of wustite surface. However, it remains unknown yet what affects the surface property of wustite.

If applying these idea to our results, it seems that reduction rates from wustite to iron \( V_w \) (g/cm\(^2\) s) (Fig. 7) have entirely good correspondence to influence of CO\textsubscript{2}/(CO+CO\textsubscript{2}) ratio in gas on swelling for three types of pellets A, B, and F at 900°C, as shown in Figs. 3(a) and 3(b).

4.3. Influence of Pellet Preparation and Binder on Swelling

Pellets D or H were indurated after pelletizing with a binder of bentonite or lime. Their addition lessened a little abnormal swelling relative to pellet A made of only iron ore, because these binders could intensify more connections between iron ore grains.

Pellets B or F were indurated or cured after pelletizing with Portland cement and then subjected to reduction tests. Pellet F has several kinds of hydrates in cement binder and these hydrates dehydrate during heating up a sample pellet until a reaction temperature to form porous structures between iron ore grains, so that pellet F could be reduced faster than pellet B as mentioned in Chap. 4.1, leading to less abnormal swelling.

Table 4 shows sulfur contents in pellets before and after partial reduction with 80%CO–20%CO\textsubscript{2} at 900°C. It was mostly found except pellet F that the conditions with \( a_S=0.1 \) increase sulfur content and the conditions with \( a_S=0 \) decrease sulfur content relative to those in non reduced pellets. The amounts of gasification of sulfur species remained in a pellet during reduction will decide the sulfur potential in gas and subsequently affect partly the reduction rate or the type of metallic iron. These findings were also reported by our previous papers.\textsuperscript{23,24}"

4.4. Actions of Sulfur Controlling the Formation of Fibrous Irons

Two categories for the favorable formation of fibrous irons caused by gaseous sulfur were supposed on the basis of sulfur adsorption on the solids.

As for wustite, sulfur adsorbs preferentially on the surface defects of wustite,\textsuperscript{25} increases the critical saturation degree of vacancy in wustite for iron nucleation \( \Delta C_v \), and diminishes the number of sites available for the iron nucleation,\textsuperscript{6} moreover, decreasing slightly the oxygen removal rate from the surface of wustite,\textsuperscript{25} to promote the chemical control as mentioned in Chap. 4.2.

As for metallic iron, sulfur adsorbs strongly on the surface of active iron forming mono atomic layer, suppresses both reactions of the oxygen removal and the deposition of iron occurring on active three phases gas/iron/wustite lines, and induces the upward growth of iron due to a larger interfacial energy between Fe/FeO with sulfur adsorption.

Table 4. Sulfur contents in pellets before and after reaction with 80%CO–20%CO\textsubscript{2} at 900°C.

| Pellet | Mass%S before reaction | Mass%S after reaction |
|--------|------------------------|----------------------|
|        | \( a_S = 0.1 \)        | \( a_S = 0 \)        |
| A      | 0.0016                 | 0.0027               | 0.0001               |
| B      | 0.0177                 | 0.0199               | 0.0077               |
| D      | 0.0014                 | 0.0053               | 0.0009               |
| F      | 0.0071                 | 0.0187               | 0.0101               |
| H      | 0.0015                 | 0.0044               | 0.0023               |

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These both behavior relating to wustite and metallic iron could have promoted the formation of fibrous irons.60

In case without sulfur, many sites are available for the iron nucleation60 and the adherence between Fe/FeO predominates to induce non whisker morphology due to a less interfacial energy between Fe/FeO.22,24

Moreover, we have previously reported a microscopic reaction mechanism for reduction of NiO pellets (a nonstoichiometric compound similarly to wustite22) with sulfur bearing reducing gas.20 These papers explained plain, porous, and fibrous iron morphology of metallic products based on difference of interfacial energy between metal and oxidies and change in rate controlling steps mainly depending on oxygen and sulfur potentials in reducing gas.

4.5. Previous Researches

Previous other researches relating to swelling are reviewed as follows. Incipently, Watanabe et al.,27 Ishimitsu et al.,28 and Fuwa et al.21 studied abnormal swelling of Marcona pellets. They clarified that abnormal swelling was brought about by the formation of iron whiskers during metallization of wustite. Fuwa et al. have found out that abnormal swelling was observed not only for Marcona pellets, but also for other kinds of iron ores.

Bleifuss,1) Ende et al.,21 Lu,3) Kasabgy et al.4) and Seaton et al.5) have investigated the influence of lime CaO on swelling. Also, Ende et al.,6) Makazawa et al.51, Lu5) and Ueda et al.7) have investigated the influence of alkali species on swelling. Most of these researches have focused to only ones such as associated with lattice defects in wustite in order to explain the mechanism of abnormal swelling along with iron whiskers. None of these researches have related the swelling to gaseous sulfur including sulfur species present in iron ore.

Recent years, Haas et al.13) and Nicolle et al.14) have observed fibrous irons when traces of gaseous sulfur is added into reducing gas. The former explained this phenomena based on influence of sulfur on carburization into reduced iron and the latter did it from change of rate limiting steps accompanied with adding sulfur.20

In this work dealing iron ore as iron source, it was recon-

4. Two types of cement bonded pellets B and F provided mostly moderate abnormal swelling independently of adding gaseous sulfur to inlet gas mixtures. Their swelling seemed to be caused by gasification of sulfur species present in cement during metallization, whose activities in gas were estimated to be around aS=2 in the reaction front from gas chromatography. However, pellet F cured with cement led to a little less abnormal swelling, probably because pellet F was reduced faster than pellet B indurated with cement.

Analogous to our previous researches using reagent iron oxides, this study using iron ore proved certainly that the existence of sulfur at low partial pressures is essential to the abnormal swelling associated with the formation of fibrous irons.

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